Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. IV. On Dihydroshonanyl Alcohol and the Optical Activity of Shonanic Acid and its Derivatives.

By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

In a previous communication,[1] the author has reported the presence of a dimethylmethylene group in the molecule of shonanic acid as a result of the investigations on the oxidation products of shonanic acid with permanganate. Next, with a view to examine the oxidation products of dihydroshonanic acid, the author attempted to prepare a sufficient quantity of the acid. But, as has been reported, the preparation of dihydroshonanic acid from shonanic acid by reduction with sodium and ethyl alcohol is always accompanied by the formation of by-products such as tetrahydroshonanic acid or isoshonanic acid, and furthermore, the separation of dihydroshonanic acid from these impurities can hardly be accomplished by the fractional distillation as there is but little difference between their boiling points. Attempt to separate it in the pure state by fractional crystallization of its metallic salts was also unsuccessful.

The author tried, hereupon, to prepare dihydroshonanyl alcohol, the unsaturated primary alcohol corresponding to dihydroshonanic acid, and to oxidise it, as such oxidation should lead to the same conclusion as might be expected from the oxidation of the dihydro-acid.

Thus, dihydroshonanyl alcohol was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol. According to H. Rupe and P. Läuger[2] the yield of camphorcarbinol increased with the molecular weight of the ester-forming radicals e.g. 10–15% by ethyl ester, 22% by isobutyl ester, 25% by isoamyl ester, 64% by β-naphthyl ester, and 94–96% by phenol ester. The present author, in order to increase the yield of the desired alcohol, prepared phenyl shonanate and reduced it with sodium and ethyl alcohol, but contrary to the expectation the yield of carbinol-compound did not improved at all.

When oxidised with chromic acid, dihydroshonanyl alcohol gave the corresponding aldehyde ($C_{10}H_{16}O$「$_1$, semicarbazone m.p. 149–150°) and

(1) This Bulletin, **12** (1937), 243.
(2) *Helv. Chim. Acta*, **3** (1920), 272.

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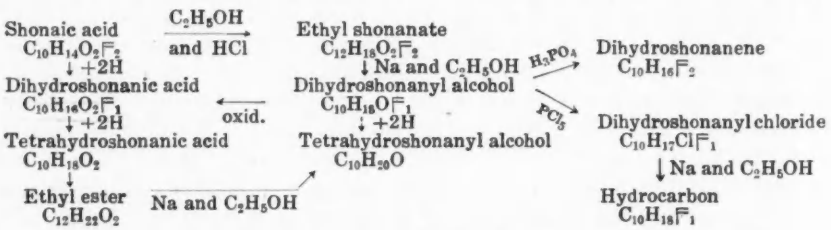
acid, and when reduced catalytically with palladium and hydrogen it afforded tetrahydroshonanyl alcohol ($C_{10}H_{20}O$), the same as obtained from ethyl tetrahydroshonanate by reduction with sodium and ethyl alcohol, which gave tetrahydroshonanic acid on oxidation. On digesting dihydroshonanyl alcohol with phosphorus pentachloride, the corresponding chloride ($C_{10}H_{17}Cl$) was obtained, which could be transformed into a hydrocarbon of the formula $C_{10}H_{18}$ by reduction with sodium and ethyl alcohol. The dehydration of shonanyl alcohol with phosphoric acid afforded a hydrocarbon $C_{10}H_{16}$ (dihydroshonanene), but the attempt to obtain its hydrochloride, nitrosochloride and nitrosite in crystalline state was not successful.

These hydrocarbons, judging from their physical properties, viz., boiling points, specific gravities and refractive indices, seem likely to be compounds of six-membered ring type, hence shonanic acid is most likely a cyclohexene derivative.

The various relations mentioned above are tabulated in the following.



About the oxidation products of dihydroshonanyl alcohol, it will be reported in the next communication.

The values of optical rotatory power exhibited by shonanic acid and its derivatives are as follows, from which it is obvious that the acid is a compound with an asymmetric carbon atom.

Shonanic acid	$[\alpha]_D^{18} = -0.74°$ (in ethyl alcohol)
Shonanic acid dibromide	$[\alpha]_D^{27} = -5.02°$ (in glacial acetic acid)
Ethyl shonate	$\alpha_D^{18} = -4.24°$
Phenyl shonanate	$\alpha_D^{28} = -2.40°$
Shonanic amide	$[\alpha]_D^{27} = -9.84°$ (in ethyl alcohol)
Dihydroshonanic acid	$\alpha_D^{30} = -1.36°$
Tetrahydroshonanic acid	$\alpha_D^{28} = -0.84°$
Ethyl tetrahydroshonanate	$\alpha_D^{28} = -0.81°$
Dihydroshonanyl alcohol	$\alpha_D^{18} = -2.24°$
Dihydroshonanyl chloride	$\alpha_D^{20} = -2.00°$
Tetrahydroshonanyl alcohol	$\alpha_D^{28} = -1.64°$
Dihydroshonanene	$\alpha_D^{28} = \pm 0°$

Experimental.

(1) **Preparation of ethyl shonanate.** 10 g. of shonanic acid together with 50 c.c. of ethyl alcohol containing 2.5% of hydrochloric acid was heated on the water-bath for an hour, the product was poured into water, extracted with ether and ethereal solution washed with water and then with dilute sodium bicarbonate solution in order to remove hydrochloric acid and unchanged shonanic acid, dried over anhydrous sodium sulphate and the solvent distilled off. The remainder was then distilled under reduced pressure when a liquid ester with the following properties was obtained. (Yield 9.3 g.) B.p. 106–108°/7 mm., 228–229°/759 mm.; d_4^{30} 0.9568; n_D^{30} 1.4674; α_D^{20} −4.24°.

(2) **Preparation of dihydroshonanyl alcohol.** 10 g. of ethyl shonanate was dissolved in 200 c.c. of absolute alcohol and 15 g. of metallic sodium was added in small portions. When all the sodium has been taken up the excess of alcohol was distilled away in vacuo and the remainder was poured into 200 c.c. of 10% sodium chloride solution. The oily matter which made appearance was taken up with ether, dried over anhydrous sodium sulphate and then the solvent was distilled off. The product amounted to 3.3 g. corresponding to 41% of the theoretical yield. Several experiments were repeated, in all of which the yield of the alcoholic substance was found to lie between 35–40% of the theoretical. Dihydroshonanyl alcohol showed the following properties: b.p. 104°/7 mm., 228–230°/765 mm.; d_4^{30} 0.9328; n_D^{30} 1.4832; α_D^{20} −2.24°; M.R. obs. 47.16, calculated for $C_{10}H_{18}O$ F 47.23. Sample (0.1379 g.) absorbed 0.1476 g. of bromine, while $C_{10}H_{18}O$F$_1$ requires 0.1433 g. The substance is readily attacked by permanganate solution in cold showing the substance is unsaturated.

(3) **Preparation of dihydroshonanyl alcohol from phenyl shonanate.** Phenyl shonanate was prepared by adding the acid chloride (9.2 g.) dissolved in 100 c.c. of petroleum ether to a solution of 4.7 g. of phenol in 10 c.c. of petroleum ether and heating the mixture on the water-bath until the evolution of hydrochloric acid gas ceased. Ether was then added to the reaction mixture and shaken with 5% sodium hydroxide solution to remove unchanged phenol. The ethereal solution was dried, the solvent distilled off, and then crude phenyl shonanate was distilled under reduced pressure. Yield 11.8 g. (97.5% of the theoretical). B.p. 153–155°/6 mm.; d_4^{30} 1.0415; n_D^{30} 1.5245; α_D^{26} −2.40°; M.R. obs. 71.16, calculated for $C_{16}H_{18}O_2$F$_5$ 71.36.

The phenol ester obtained above (11.8 g.) was dissolved in 120 c.c. of absolute alcohol and was reduced with 9 g. of sodium in the usual manner when 2.2 g. of the corresponding alcohol was obtained, the yield amounting to 29.5% of the theoretical. The yield of the carbinol was 27% and 29% of the theoretical respectively when the reduction was carried out by using smaller (6.5 g.) and larger (11 g.) proportions of metallic sodium. The physical properties of the dihydroshonanyl alcohol are as follows: b.p. 103–103.5°/6 mm.; d_4^{30} 0.9319; n_D^{30} 1.4826; α_D^{24} −2.09°.

(4) **Hydrogen dihydroshonanyl phthalate.** When heated with equivalent weight of phthalic anhydride in benzene solution dihydroshonanyl alcohol gave its acid phthalic ester. From 1 g. of the sample, 1 g. of phthalic anhydride and 2 c.c. of benzene, the acid phthalic ester was obtained in prismatic needles, which melted at 124° after a recrystallization from ethyl alcohol.

(5) **Oxidation of dihydroshonanyl alcohol with chromic acid.** 10 g. of the alcohol dissolved in 150 c.c. of glacial acetic acid was kept at 10–15° and a solution of chromic acid (10 g.) in a little water and glacial acetic acid (50 c.c.) was added drop by drop with constant stirring. After all the chromic acid solution has been consumed the reaction mixture was warmed on the water-bath at 50–60° for 30 minutes. The reaction mixture was then poured into water and aldehydic and acidic substances were extracted and separated as usual.

(a) *The aldehyde* showed the following properties: b.p. 107–110°/18 mm.; d_4^{30} 0.9630; n_D^{30} 1.4833; M.R. obs. 45.10, calculated for $C_{10}H_{16}O$ 45.78. The substance was a colourless mobile oil with pleasant odour and on testing with Schiff's reagent and Tollens' solution it showed the characteristic reactions of aldehyde.

Semicarbazone. A mixture of 1 g. of the sample, 0.8 g. of semicarbazide hydrochloride and 0.6 g. of sodium bicarbonate afforded a semicarbazone as glistening leaflets melting at 149–150° after recrystallizations from ethyl alcohol. (Found: N, 20.88. Calculated for $C_{11}H_{19}ON_3$: N, 20.10%.)

(b) *The acidic substance* showed the following properties: b.p. 132°/5 mm., d_4^{30} 1.022; n_D^{30} 1.4804; M.R. obs. 46.74, calculated for $C_{10}H_{16}O_2$ 47.30. It decolourized permanganate and bromine in cold showing its unsaturated nature. Sample (0.204 g.) absorbed 0.187 g. of bromine, while $C_{10}H_{16}O_2$ requires 0.194 g.

Amide. The amide was prepared by the interaction of the acid chloride and aqueous ammonia. It was glistening scales melting at 130° when recrystallized from 60% ethyl alcohol and was found to be identical by melting in admixture with dihydroshonanic amide.

(6) **Preparation of dihydroshonanyl chloride.** When dihydroshonanyl alcohol (3 g. in 10 c.c. of petroleum ether) was treated with phosphorus pentachloride (6.8 g.), the chloride with the following properties was obtained: b.p. 87°/13 mm.; d_4^{30} 0.9984; n_D^{30} 1.4900; α_D^{20} −2.00°; M.R. obs. 49.95, calculated for $C_{10}H_{17}Cl$ 50.54. At the end of the distillation the hydrocarbon of the following properties came over but its detailed examination was impossible owing to the scarcity of the material. B.p. 172–174°/757 mm.; d_4^{30} 0.8678; n_D^{30} 1.4730. (Found: C, 87.49; H, 12.04. Calculated for $C_{10}H_{16}$: C, 88.22; H, 11.78%.)

(7) **Preparation of hydrocarbon $C_{10}H_{18}$ from dihydroshonanyl chloride.** The chloride (3 g.) mentioned above was dissolved in 50 c.c. of absolute alcohol and 4 g. of metallic sodium was added in small portions. The reaction mixture was then heated on the water-bath and poured into a bulk of water and the hydrocarbon deposited was taken up with ether. The ethereal solution was dried over anhydrous sodium sulphate and the remainder after removal of the solvent was fractionally distilled under the ordinary pressure.

(1) B.p. 163–165° 0.2 c.c.; (2) B.p. 165–166° 1.3 c.c.; (3) B.p. 166–168° 0.3 c.c. The main fraction (2) showed the following properties: d_4^{30} 0.8401; n_D^{30} 1.4658; α_D^{26} +0.40°; M.R. obs. 45.48, calculated for $C_{10}H_{18}$ 45.60. (Found: C, 87.18; H, 13.14. Calculated for $C_{10}H_{18}$: C, 86.96; H, 13.04%.)

(8) **Dehydration of dihydroshonanyl alcohol.** 5 g. of dihydroshonanyl alcohol was heated with 20 g. of phosphoric acid at 200–210° for an hour. The reaction mixture was then poured into water and the oily substance was extracted with ether.

The ethereal solution was next heated with 1 g. of metallic sodium on the water-bath in order to recover the unchanged alcohol and the solvent was distilled off. The extract was then subjected to fractional distillation under the ordinary pressure over metallic sodium. The main fraction showed the following properties: b.p. 168–169°/759 mm.; d_4^{30} 0.8630; n_D^{30} 1.4870; α_D nil; M.R. obs. 45.32, calculated for $C_{10}H_{16}$ 1 45.20. (Found: C, 88.28; H, 11.42. Calculated for $C_{10}H_{16}$: C, 88.23; H, 11.77%.)

(9) **Preparation of tetrahydroshonanyl alcohol.** Tetrahydroshonanyl alcohol was obtained by catalytic reduction of dihydroshonanyl alcohol on the one hand and by reducing tetrahydroshonanate with sodium and ethyl alcohol on the other.

(a) *Catalytic reduction of dihydroshonanyl alcohol.* 4.438 g. of dihydroshonanyl alcohol, dissolved in 40 c.c. of ethyl alcohol, was catalytically reduced by hydrogen and palladium. Hydrogen absorbed: 644 c.c. (0°, 760 mm.); calculated for $C_{10}H_{18}O$ 1: 645 c.c. (0°, 760 mm.). The product showed the following properties: b.p. 100–101°/7 mm.; d_4^{30} 0.9253; n_D^{30} 1.4764; α_D^{28} −1.64°; M.R. obs. 47.57, calculated for $C_{10}H_{20}O$ 47.52.

(b) *The reduction of ethyl tetrahydroshonanate with sodium and ethyl alcohol.* 5 g. of ethyl tetrahydroshonanate was dissolved in 150 c.c. of absolute alcohol and was reduced by 8 g. of sodium. The alcoholic substance produced showed the following properties, in good accord with those of the product of (a). B.p. 102°/8 mm.; d_4^{30} 0.9250; n_D^{20} 1.4761; α_D^{24} −1.68°; M.R. obs. 47.57, calculated for $C_{10}H_{20}O$ 47.52.

(10) **Oxidation of tetrahydroshonanyl alcohol with chromic acid.** To a solution of 3 g. of tetrahydroshonanyl alcohol in 70 c.c. of glacial acetic acid, 3 g. of chromic acid was added in small portions with vigorous stirring. The acid produced had the following properties (Yield 1.2 g.): b.p. 120°/2 mm.; d_4^{30} 0.9876; n_D^{30} 1.4650; α_D^{26} −0.84°; M.R. obs. 47.60, calculated for $C_{10}H_{18}O_2$ 47.70.

Amide. The amide prepared from 1 g. of the acid chloride and aqueous ammonia melted at 144° after recrystallization from 60% ethyl alcohol, which showed no depression of the melting point when mixed with an authentic specimen of tetrahydroshonanic amide.

In conclusion, the author wishes to express his sincere thanks to Prof. Kinzô Kafuku for his kind guidance.

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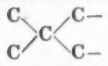
Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. V. Studies on the Oxidation of Dihydroshonanyl Alcohol and the Ozonolysis of Shonanic Acid.

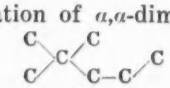
By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

It was reported in the previous communications that the molecule of shonanic acid contains a linkage  as shown by the products of oxidation with potassium permanganate,[1] and that the elevation of boiling point accompanying its isomerisation to isoshonanic acid may be attributed to the migration of the semicyclic double bond into the ring system.[2]

Now, with a view to ascertain the presence of a semicyclic double bond and hence to establish the constitutional formula of shonanic acid, the author examined its ozonolysis as well as the oxidation of dihydroshonanyl alcohol with potassium permanganate, and was able to formulate further arrangement of atoms in the molecule of shonanic acid.

The ozonisation of shonanic acid gave a crystalline mono-ozonide, which on treatment with water gave an unsaturated acid of the formula $C_9H_{14}O_3$. This acid was found to be an unsaturated aldehydic acid and hence on further oxidation with hydrogen peroxide it gave an unsaturated dibasic acid of the formula $C_9H_{14}O_4$. The methyl ester of this dibasic acid was prepared, which on ozonolysis gave formaldehyde, formic acid and an acidic substance, which on treatment with dilute nitric acid gave dimethylmalonic acid and *asym*-dimethylsuccinic acid. When dihydroshonanyl alcohol was oxidised with dilute permanganate and then with dilute nitric acid, oxalic, *asym*-dimethylsuccinic and *a,a*-dimethylglutaric acids were produced.

The formation of *a,a*-dimethylglutaric acid reveals the presence of arrangement  in the molecule of dihydroshonanyl alcohol. As dihydroshonanyl alcohol is the alcohol derived from dihydro-

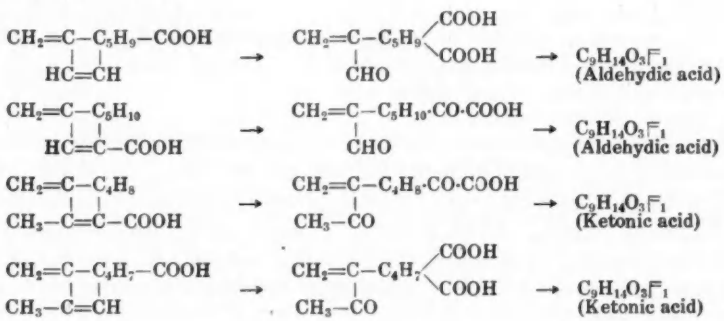
(1) This Bulletin, **12** (1937), 243.
(2) *Ibid.*, **11** (1936), 759.

shonanic acid, the conclusions about its constitution may directly be adopted to dihydroshonanic, as well as to shonanic acid.

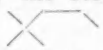
From considerations of the oxidation products mentioned above, the author has come to the following conclusions.

(1) The formation of mono-ozonide shows that the double bonds in shonanic acid are conjugated.[3]

(2) The formation of the unsaturated aldehydic acid $C_9H_{14}O_3$ cannot be explained unless the formation of the mono-ozonide takes place at the ring-forming double bond, and by presuming the ring fission to occur at this spot, this double bond must have existed either in the form $-\overset{|}{\underset{H}{C}}=\overset{|}{\underset{H}{C}}-$ or $-\overset{|}{\underset{H}{C}}=\overset{|}{\underset{COOH}{C}}-$, otherwise the formation of the aldehydic acid becomes impossible.

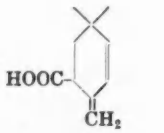


(3) The formation of formaldehyde and formic acid by ozonolysis of the methyl ester of the unsaturated dibasic acid $C_9H_{14}O_4$ shows the presence of a semicyclic double bond attached to the nucleus.

Now the data for the establishment of the structural formula of shonanic acid are almost complete. (I) Shonanic acid contains a six-membered carbon ring,—proved by the formation of dinitrobenzene.[1] (II) It has within itself a skeleton  . (III) It has an exocyclic double bond attached to the ring. (IV) It has the second ethylenic linkage which is conjugated to the exocyclic one. (V) It has a carboxylic group.

By putting these facts together, it remains now to determine the position of $=CH_2$ and $-COOH$ and the second ethylenic linkage in the dimethylcyclohexene nucleus. Thus there are 12 cases which fulfil the above requirements, viz.:

(3) Houben-Weyl, "Die Methoden der organischen Chemie," 3. Aufl., Bd. III, 409, 454.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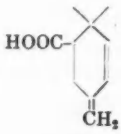
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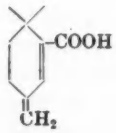
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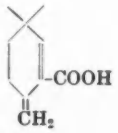
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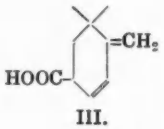
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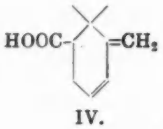
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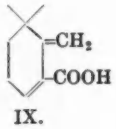
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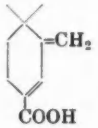
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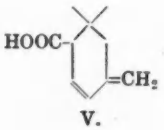
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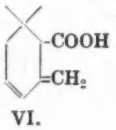
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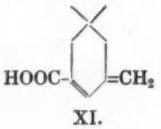
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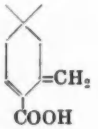
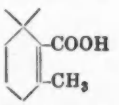
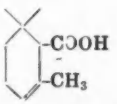
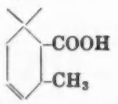
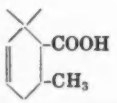

XII.

Among these formulæ those without an asymmetric carbon atom must be excluded as shonanic acid is optically active. Thus the formulæ I–VI remain to be inspected. And furthermore VI should be excluded for the following reason. If VI denotes shonanic acid, dihydroshonanic acid should be identical with one of the following substances, whereas dihydroshonanic acid proves to be a distinctly different substance.


β-Cyclogeranic acid[4] m.p. 93–94°


α-Cyclogeranic acid[5] m.p. 106°


Δ^3-Cyclogeranic acid[6] m.p. 75–76° or 83–84°


Δ^4-Cyclogeranic acid[7] m.p. 102–102.5°

Thus it follows that one of the first five formulæ (I–V) should represent the constitution of shonanic acid.

Experimental.

I. Oxidation of dihydroshonanyl alcohol.

The substance was prepared from ethyl shonanate by reduction with sodium and ethyl alcohol as previously reported.[8] It showed the following properties: b.p. 103–

(4) Tiemann, *Ber.*, **33** (1900), 3723.
(5) Tiemann, *Ber.*, **31** (1898), 827.
(6) Merling, *Ber.*, **41** (1908), 2066.
(7) Merling, *Chem. Zentr.*, **77** (1906), II, 1694.
(8) This Bulletin, **12** (1937), 253.

104°/7 mm., 229°/760 mm.; d_4^{30} 0.9328; n_D^{30} 1.4832; α_D^{18} −2.24°; M.R. obs. 47.17, calculated for $C_{10}H_{18}O\Gamma_1$ 47.12.

20 g. of the substance was mixed with 1000 c.c. of 2% sodium hydroxide solution and then 3000 c.c. of 3.2% potassium permanganate solution was added drop by drop with vigorous stirring, the temperature of the reaction mixture being maintained at 20–25°. After all the permanganate had been consumed, the reaction mixture was saturated with carbon dioxide, and then warmed on the water-bath at 40–50° for an hour. Manganese dioxide precipitated was filtered off while hot and the filtrate was evaporated on the water-bath nearly to dryness and was acidified with dilute sulphuric acid. The organic acid set free was extracted with ether and dried over anhydrous sodium sulphate. After distilling off the solvent, there remained a sticky, slightly yellowish liquid, which amounted to 15 g. The substance was acidic, sparingly soluble in water and gradually acquired reddish yellow tint on exposure to the air. It was then warmed with 400 c.c. of dilute nitric acid (d = 1.12), evaporated on the water-bath, and ultimately under reduced pressure to remove traces of nitric acid present. The product thus obtained was a pale yellow viscous substance which was difficultly soluble in ether, chloroform and petroleum ether, but soluble in water, alcohol and warm benzene. On testing it with Schiff's reagent and Tollens' solution it proved to be perfectly free from aldehyde. On standing in cold some crystalline substance made appearance, which was spread over a porous plate previously cooled in an ice-box and stood over night in cold in order to remove the adhering fluid matter. The crystalline substance, which amounted to 7 g., was a colourless powder melting at 73–118° without any purification. The liquid portion absorbed by the porous plate was recovered by extracting it with ether, the details of which are described later.

(1) **Investigation of crystalline substances.** (a) *Oxalic acid.* The crystalline substance (7 g.) obtained above was boiled with 30 c.c. of chloroform, filtered while hot, washed with chloroform and dried in vacuo. It showed a m.p. 96–99°. On recrystallization from hot water it was obtained in colourless needles melting at 101°. It was identified as oxalic acid by mixed melting point.

(b) asym-*Dimethylsuccinic acid.* The above filtrate, on evaporating chloroform deposited a white crystalline powder melting at 133°. This was boiled with a little water and after quenching, needle crystals of oxalic acid were filtered off. The filtrate was evaporated and then cooled with freezing mixture, when prismatic needles with m.p. 134–136° were obtained. Another recrystallization from benzene furnished colourless needles melting at 139°. The substance was soluble in water, alcohol, benzene and chloroform. Acid value 767.4, calculated for $C_6H_{10}O_4$ 767.1. (Found: C, 48.87; H, 6.82. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%. Analysis of the silver salt: Ag, 60.02. Calculated for $C_6H_8O_4Ag_2$: Ag, 59.97%.)

Among the acids represented by $C_6H_{10}O_4$, *asym*-dimethylsuccinic acid melts at the same temperature (139–140°) as the substance under investigation, whose identity with the former was confirmed by observing the melting point of the mixture.[9]

(9) *asym*-Dimethylsuccinic acid used for the trial was prepared by oxidation of dimethyl-dihydroresorcin according to the description of Vorländer and Gärtner [*Ann.*, **304** (1899), 5, 15].

(2) **Investigation of the liquid portion.** The liquid portion was recovered by extracting the porous plate broken into small bits with ether. The substance thus recovered was a viscous fluid with yellowish tint and amounted to 7.3 g. As the purification by vacuum distillation was ineffective, it was esterified by boiling it with 40 c.c. of ethyl alcohol containing 6% hydrochloric acid and the ester thus prepared was fractionated in vacuo.

(a) *Acetic acid.* As the ethyl alcohol recovered from the esterification mixture smelled of ethyl acetate, it was boiled with 5 c.c. of 50% potassium hydroxide solution under reflux condenser, and the remainder after removal of alcohol was evaporated nearly to dryness and acidified with 5N sulphuric acid and extracted with ether. From the ethereal solution about 0.8 g. of liquid acidic substance bearing the characteristic odour of acetic acid was obtained. The silver salt prepared from its neutralized solution contained 64.65% of the silver agreeing well with the theoretical silver content of the silver acetate.

(b) *α,α-Dimethylglutaric acid.* The ester portion thus obtained was dissolved in ether, washed with water and 5% sodium hydroxide solution successively in order to remove any traces of ethyl alcohol and unchanged acidic substances, dried over anhydrous sodium sulphate and the solvent was distilled off. The reddish brown matter remaining behind amounted to ca. 8 g., which was fractionally distilled under 10 mm.

Fr. No.	B.p.	Wt.(g.)
1	80–86°/10 mm.	1.2
2	86–95°/10 mm.	0.7
3	95–105°/10 mm.	—
4	105–107°/10 mm.	4.0
5	107°/10 mm.—105°/3 mm.	1.0
6	105–135°/3 mm.	0.6

Fraction 1 had the following properties: b.p. 185–187°/770 mm.; d_4^{20} 1.088; n_D^{20} 1.4160; M.R. obs. 33.67, calculated for $C_6H_{10}O_4$ 33.10. (Found: C, 49.08; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The physical constants of the fraction agree well with those of diethyl oxalate (b.p. 186°/755 mm.; d_4^{20} 1.0793; n_D^{20} 1.4104)[10] and the free acid obtained by saponification melted at 101°, which was found to be identical with oxalic acid melting in admixture with authentic specimen.

Fraction 4 had the following properties: b.p. 233–235°/770 mm.; d_4^{20} 0.9956; n_D^{20} 1.4293; M.R. obs. 55.97, calculated for $C_{11}H_{20}O_4$ 56.42. (Found: C, 61.07; H, 9.21. Calculated for $C_{10}H_{20}O_4$: C, 61.11; H, 9.26%.) The analytical data showed that the substance represents a compound corresponding to the diethyl ester of a dibasic acid of the formula $C_7H_{12}O_4$. The substance was saponified by warming 3 g. of the sample with 2 g. of potassium hydroxide, 8 c.c. of water and 100 c.c. of ethyl alcohol for an

(10) Delfes, *Jahresbericht über die Fortschritte der Chemie*, **1854**, 26; Brühl, *Ann.*, **203** (1880), 27.

hour. The excess of alcohol was distilled off and the remainder was evaporated to a smaller bulk and was acidified with dilute hydrochloric acid and the organic acid thus set free was extracted 4 times with chloroform using 10 c.c. each time. The chloroform solution was collected, dried over anhydrous sodium sulphate and the solvent distilled off. The sticky liquid acid remaining behind was then warmed with 5 c.c. of conc. hydrochloric acid and then cooled with freezing mixture, when the substance became crystalline and melted at 67°. It was purified twice by precipitation from benzene solution with the addition of light petroleum ether. Thus its melting point attained 83°. (Found: C, 52.29; H, 7.56. Calculated for $C_7H_{12}O_4$: C, 52.50; H, 7.50%.) It is clear that the acid under investigation is a dibasic acid of the formula $C_7H_{12}O_4$ and the melting point of the sample is proximate to those of α,α-dimethylglutaric acid[11] (m.p. 83–84°, diethyl ester b.p. 235–236°), α,β-dimethylglutaric acid[12] (m.p. 84–84.5°) or *d*-β-methyladipic acid[13] (m.p. 84.5°). Among these three acids *d*-β-methyladipic acid can be excluded for the reason that it is insoluble in cold benzene, and furthermore its diethyl ester has a quite different boiling point[14] (b.p. 257°) from that of the diethyl ester in question. Reminding that dimethylmalonic acid and *asym*-dimethylsuccinic acid were found among the oxidation products of shonanic acid and dihydroshonanyl alcohol respectively, it should be expected that the present dibasic acid is α,α-dimethylglutaric acid. Now, it was found to be identical with α,α-dimethylglutaric acid by examining the melting point in admixture with the authentic sample prepared from ionone by oxidation as described by Tiemann.[15]

II. Ozonolysis of shonanic acid.

(1) **Preparation of mono-ozonide of shonanic acid.** To a well-cooled solution of the acid (10 g.) dissolved in carbon tetrachloride (100 c.c.), a current of ozonized oxygen containing ca. 3% ozone was passed through at a rate of 15–20 liters per hour until the absorption of ozone has ceased. The ozonide obtained was crystalline and floated on the surface of the solvent, which was filtered off, washed several times with carbon tetrachloride, spread over porous plate to remove the adhering solvent and finally dried in vacuo. The yield of the ozonide amounted to about 12 g., which is approximately the theoretical value calculated as mono-ozonide ($C_{10}H_{14}O_2{\cdot}O_3$). The mono-ozonide showed the decomposition point 82° and when perfectly dry it decomposed vigorously with evolution of heat. It was quite insoluble in chloroform, benzene, carbon tetrachloride and ether, and was attacked very slowly by water at ordinary temperature but more rapidly at elevated temperature (above 60°).

(2) **Decomposition of the ozonide.** The ozonide was gently heated on the water-bath at about 75° with 5 times of its volume of water in a current of hydrogen and the decomposition products thus obtained were examined. The hydrogen gas escaping from the decomposition flask was introduced into ice-cold distilled water

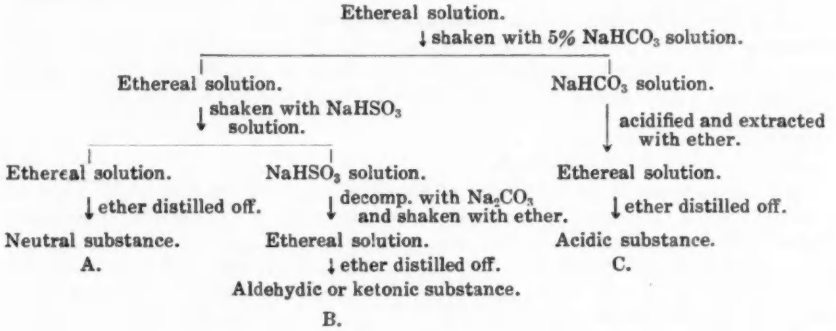
(11) Kishner, *Chem. Zentr.*, **79** (1908), II, 1859; Blaise, *Bull. soc. chim.*, [3], **21** (1899), 626.
(12) Blaise, *Bull. soc. chim.*, [3], **29** (1903), 333.
(13) Semmler, *Ber.*, **25** (1892), 3516.
(14) Markownikow, *Chem. Zentr.*, **74** (1903), II, 288.
(15) Tiemann, *Ber.*, **31** (1898), 862.

in order to catch any soluble matter produced, and then into a saturated solution of barium hydroxide. Carbon dioxide was evolved and precipitated barium carbonate, which amounted to ca. 3.8 g. per 10 g. of the ozonide.

When the decomposition was over the presence of aldehydic substance in the water trap was tested with Schiff's reagent as well as with Tollens' solution which gave negative results. The iodoform reaction was also negative.

The oily product remaining in the decomposition flask was distilled in steam, and the distillate gave positive reaction with Schiff's reagent as well as with Tollens' solution whilst it gave no iodoform reaction showing the absence of acetone or acetaldehyde therein. The dimedon test was also thoroughly negative, showing the absence of formaldehyde in the distillate. The strong positive aldehydic reaction shown even by the first running may be attributed to the very nature of the product in question.

The product which came over with steam was then extracted with ether and was treated according to the following scheme.



Finally the substance was found to accumulate in C, and the portions going to A or B very minute.

(3) **The investigation of the acidic substance (C).** The yield of the acidic substance amounted to 24 g. from 50 g. of the ozonide. It showed all the characteristic properties of an aldehyde but the attempt to obtain its semicarbazone in crystalline state was not successful. As the purification of the substance by distillation in vacuo was not attained, the aldehyde group present was first oxidised to acid group, the resulting acid esterified and the ester fractionated in vacuo. The substance thus purified was subjected to more minute examinations.

Oxidation of the aldehydic acid. 20 g. of the aldehydic acid was dissolved in 200 c.c. of 10% sodium hydroxide solution and was oxidised with 22 c.c. of perhydrol (30%) at 40–45°, when the reddish colour of the solution changed gradually to a yellowish tint, and the solution gave no more positive result with Tollens' solution. The solution was then evaporated to a smaller bulk in an atmosphere of carbon dioxide, acidified with dilute sulphuric acid and the organic acid thus liberated was extracted with ether. Yield 16 g.

Preparation of the methyl ester. The acid obtained above was esterified by heating with 100 g. of methyl alcohol containing 3% hydrochloric acid on the water-bath for 2 hours and the product was extracted as usual and fractionally distilled under reduced pressure.

Fr. 1	b.p. 86–109°/19 mm.	3 c.c.
2	b.p. 109°/19 mm.–142°/7 mm.	9 c.c.
3	b.p. 142–147°/7 mm.	4 c.c.

The main fraction (2) was once more rectified when it showed the following properties. (Yield 7 c.c.) B.p. 138–140°/7 mm.; d_4^{30} 1.073; n_D^{30} 1.4733. (Found: C, 61.57; H, 8.52. Calculated for $C_{11}H_{18}O_4$: C, 61.68; H, 8.41%.)

The substance was undoubtedly unsaturated since it absorbed bromine and decolourlized permanganate solution in cold. Its empirical formula corresponded with $C_{2.7}H_{4.6}O$, but since it is a dimethyl ester of a dibasic acid, it must contain two $COOCH_3$ groups. It naturally follows that the formula of this acid should be $(C_{2.7}H_{4.6}O)_4$ or $C_{11}H_{18}O_4$ approximately. The experimental data concerning the molecular weight agreed fairly well with this formula, viz.: 0.2577 g. subst. absorbed 0.1856 g. of bromine, while $C_{11}H_{18}O_4$ requires 0.1927 g. 0.3858 g. subst. absorbed 45.1 c.c. of hydrogen (0°, 760 mm.), while $C_{11}H_{18}O_4$ requires 40.4 c.c. Saponification value 517.8, calculated for $C_{11}H_{18}O_4$ 523.4. Thus the free acid should be represented by $C_9H_{14}O_4$[16] or $C_7H_{12}(COOH)_2$, and the foregoing aldehydic acid by $C_9H_{14}O_3$ or $C_7H_{12}\begin{matrix}CHO\\COOH,\end{matrix}$ presumably aliphatic with one ethylenic linkage. The position of the double bond was determined by ozonolysis of the dimethyl ester of the former.

(4) **Ozonolysis of dimethyl ester of the acid $C_9H_{14}O_4$.** The methyl ester (10 g.) was dissolved in carbon tetrachloride (100 c.c.) and 3% ozonized oxygen made to bubble through until the solution became inactive against bromine. At the end of the reaction the solution was heated in a flask with 50 c.c. of water on the water-bath in a current of CO_2-free air and made to distil slowly. The decomposition of the ozonide set in with the distillation of carbon tetrachloride. In order to catch any water soluble substance such as formaldehyde, acetaldehyde or acetone, which may have been produced during the decomposition of the ozonide, a gas-washer containing a little water was put in place of the receiver and the air escaping out of this receiver was once more introduced into another gas-washer with a little water and then into barium hydroxide solution to detect carbon dioxide.

Carbon dioxide. The formation of carbon dioxide was recognized by the formation of barium carbonate in the gas-washer.

Formaldehyde. The water and carbon tetrachloride in the gas-washer was separated and the aqueous layer tested with Schiff's reagent as well as with Tollens' solution. When 8 c.c. of the aqueous distillate was mixed with 5 c.c. of alcoholic dimedon solution (10%) needle crystals of formaldimedon made appearance, which was filtered off, washed with water, and dried. It melted at 185°, and another recrystallization from alcohol furnished colourless needles melting at 191° alone and

(16) Fenton and Sisson, *J. Chem. Soc.*, **91** (1907), 690.

in admixture with pure specimen of formaldimedon. Thus the presence of formaldehyde was recognized.

Identification of formic acid. The residual liquid product in the decomposition flask was then extracted with ether and was saponified with alcoholic potash. The resulting acidic substance gave positive reaction with Schiff's reagent as well as Tollens' solution and it deposited mercurous chloride when heated with concentrated mercuric chloride solution.

The liquid acid obtained (8 g.) was stirred 3 times with 10 c.c. of water each time for about an hour and the water layer separated was neutralized with aqueous ammonia and evaporated to ca. 10 c.c. A portion of this solution when heated with mercuric chloride solution deposited mercurous chloride, while it showed a reducing action on Tollens' solution. The neutral solution was acidified with dilute hydrochloric acid and was extracted with ether several times.

The ethereal solution thus obtained was then mixed with about 10 c.c. of water and warmed on the water-bath and the ether was expelled. The residual aqueous solution was digested with magnesium powder at ordinary temperature and filtered.[18] From the filtrate on mixing with alcoholic dimedon solution, formaldimedon melting at 191° was obtained, which shows that the original solution contained formic acid.

Oxidation of the liquid acid obtained from the ozonide. The liquid acidic substance, after removal of formic acid, amounted to 6.5 g. It was warmed with 320 c.c. of dilute nitric acid (d = 1.12) on the boiling water-bath for 5 hours and then evaporated to syrup and extracted with ether. From the ethereal solution an oily substance was precipitated by the addition of light petroleum ether, which gradually turned into a crystalline mass on cooling. The mass softened at 111° and melted at 131° without any purification. By fractional recrystallization from a mixture of light petroleum ether and benzene (2:3) two kinds of crystalline acids were obtained, the one crystallizing at first melted at 123–129° and the other at 173–178° (with decomposition). By three successive purifications from the same solvent two acids with m.p. 139° and m.p. 186–187° (with decomp.) were obtained. The former had the formula $C_6H_{10}O_4$ and was identified as *asym*-dimethylsuccinic acid by melting in admixture with an authentic specimen. (Found: C, 49.12; H, 6.89. Calculated for $C_6H_{10}O_4$: C, 49.32; H, 6.85%.) The latter melting at 186–187° (with decomp.) had the composition $C_5H_8O_4$ and was found to be identical with dimethylmalonic acid by examining the melting point of the mixture of the sample with an authentic specimen.

In conclusion, the author wishes to thank Prof. K. Kafuku for his kind advices and suggestions rendered during the course of this work.

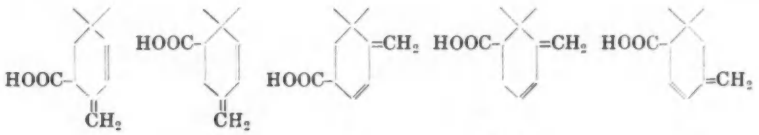
Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. VI. Studies on the Oxidation of Dihydroshonanic Acid with Ozone and Potassium Permanganate.

By Nobutoshi ICHIKAWA.

(Received November 24th, 1936.)

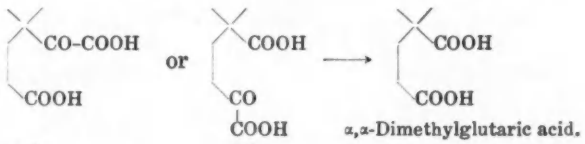
In the previous communication the author has reported that the constitution of shonanic acid should be represented by one of the following formulæ:



I. II. III. IV. V.

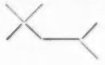
The present communication deals with the studies on the oxidation products of dihydroshonanic acid with ozone and potassium permanganate and as a result of these investigations the author has come to the conclusion that the acid must be represented by the formula III.

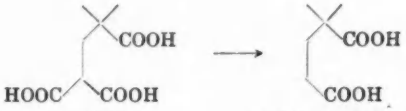
The ozonisation of dihydroshonanic acid and the subsequent decomposition of the ozonide, followed by the treatment with dilute nitric acid, furnished a dibasic ketonic acid of the formula $C_8H_{12}O_5$, which on further oxidation with perhydrol gave α,α-dimethylglutaric acid. These facts show that this dibasic ketonic acid may be represented by either VI or VII.



VI. VII. α,α-Dimethylglutaric acid.

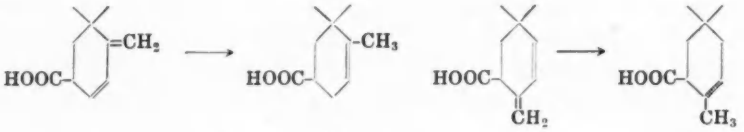
The oxidation of dihydroshonanic acid with potassium permanganate gave a crystalline dihydroxy-dihydroshonanic acid $C_{10}H_{18}O_4$ (m.p. 161–161.5°) together with a liquid dibasic ketonic acid with the formula $C_{10}H_{16}O_5$. On examination, the latter proved to be a chain compound and its optical activity revealed the presence of at least one asymmetric

carbon atom. It could be prepared from the former by oxidizing it with lead tetracetate as described by R. Criegee, L. Kraft and B. Rank[1] and subjecting the resulting aldehydic acid to the action of alkaline perhydrol. The ketonic acid was evidently a methyl ketonic acid as it could be converted into tribasic acid $C_9H_{14}O_6$ by digestion with sodium hypochlorite. This tribasic acid, on oxidation with dilute nitric acid, gave α,α-dimethylglutaric acid and another tribasic acid of the formula $C_8H_{12}O_6$, which was easily transformed into α,α-dimethylglutaric acid on treatment with hot concentrated hydrochloric acid. It naturally follows that the tribasic acid $C_8H_{12}O_6$ should be represented by VIII and as consequence an arrangement  in the molecule of dihydroshonanic acid is to be expected.



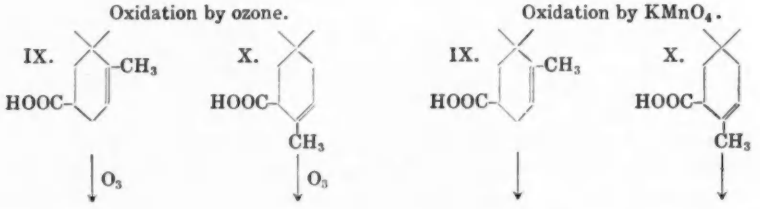
VIII. α,α-Dimethylglutaric acid.

There are two possible constitutional formulæ for dihydroshonanic acid which are capable of explaining the facts mentioned above, the one is IX which should be derived from III while the other is X transformed from I.

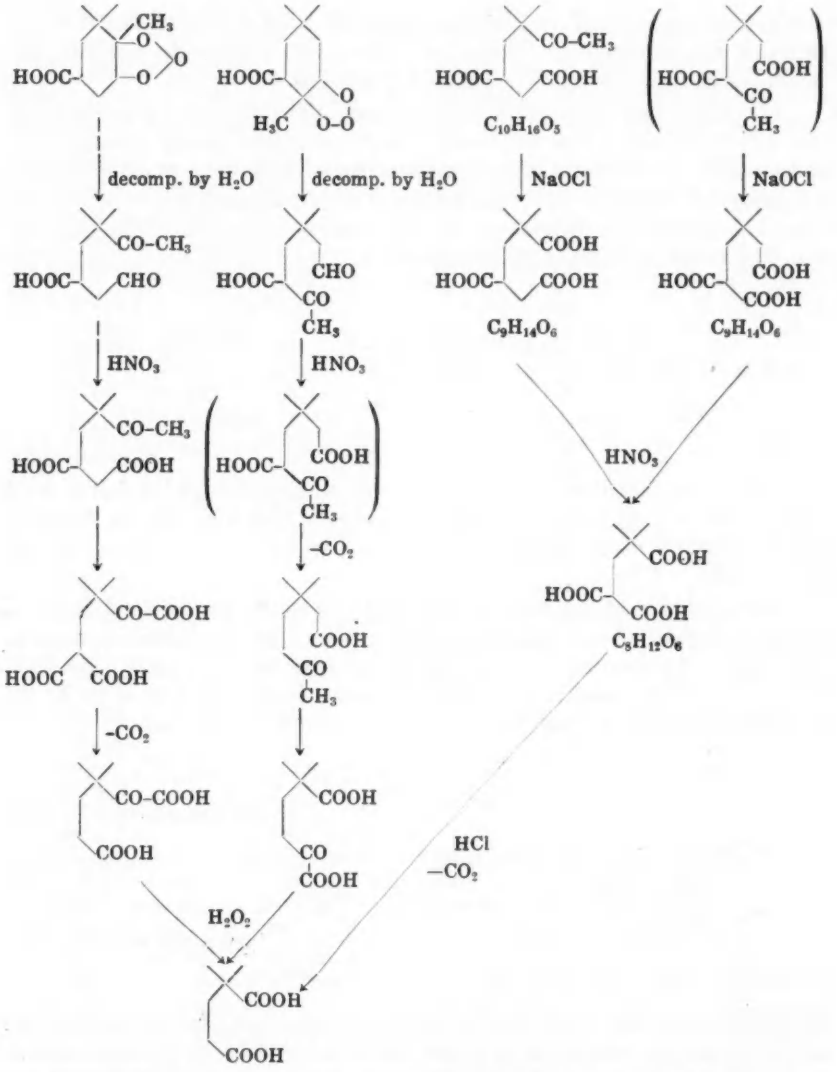


III. IX. I. X.

Oxidation by ozone. Oxidation by $KMnO_4$.



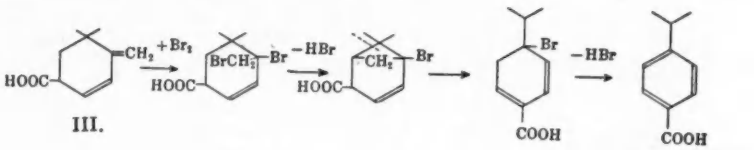
(1) *Ann.*, **507** (1933), 159.



The compound put in parentheses may not exist as free acid as it is a β-ketonic acid and consequently may transform into monoketo-monocarboxylic acid of the formula $C_9H_{16}O_3$ with liberation of carbon dioxide. For this reason the formula X seems not suitable for the constitution

of dihydroshonanic acid, whilst the constitution IX fulfils all the requirements of this compound. Now, the author will choose the formula III for shonanic acid by the two following reasons.

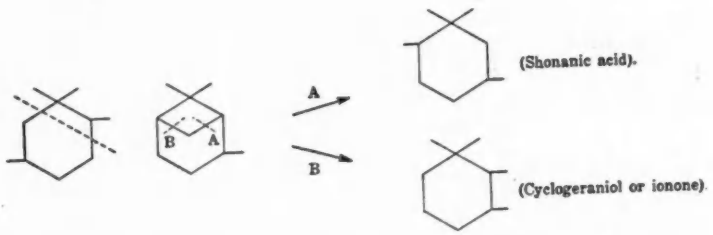
(1) The fact that by distillation under reduced pressure shonanic acid dibromide gives rise to *p*-cuminic acid, can very easily be explained by assuming the formula III as shown by the following scheme (as for the mode of addition of bromine see the second paper[2]), while the formula I necessitates to assume an extravagant migration of the carboxyl group in order to explain this conversion.



III. *p*-Cuminic acid

(2) The fact that shonanic acid can be esterified with fairly good yield (from 10 g. of the acid 9.3 g. of the ester), indicates that in shonanic acid the carbon atom in the ortho-position to its carboxyl group is unsubstituted.

The skeleton of III may be regarded as consisting of two isoprene nuclei as shown below whilst this structure may be considered as derived from pinane by cleavage of four-membered ring system at A. It is noteworthy that if the splitting of the four-membered ring occurs at B, the resulting skeleton represents that of cyclogeraniol or ionone.



Attention must also be drawn to the interesting fact that an acid of the structure closely related to pinene, the most widely distributed constituent of various essential oils, especially in those of coniferous trees, was found as the prevailing constituent of the conifer *"Libocedrus formosana,* Florin" or "Shônan-Boku".

(2) This Bulletin, **12** (1937), 233.

Experimental.

I. Separation of dihydroshonanic acid. Dihydroshonanic acid was separated by fractionation of the acidic portion obtained as by-product during the preparation of dihydroshonanyl alcohol by the reduction of ethyl shonanate with sodium and ethyl alcohol (see the fourth paper[3]).

140 g. of the material was subjected to fractional distillation under reduced pressure using Widmer's fractionating column. After three successive rectifications, the following fractions were obtained.

Fr. No.	B.p./6 mm.	d_4^{20}	n_D^{30}	α_D^{20}	Wt.(g.)	Wt.(%)
1	–137°	—	1.4796	—	3	2.17
2	137–138°	1.007	1.4798	−5.28°	43	31.16
3	138–139°	1.012	1.4800	−5.20°	32	23.19
4	139–140°	1.012	1.4810	−5.20°	18	13.04
5	140–141°	1.015	1.4824	−4.68°	7	5.07
6	141–144°	1.017	1.4834	−3.68°	4	2.90
7	144–147°	Crystallized	—	—	12	8.69
8	147–150°	,,	—	—	14	10.14
9	Residue				5	3.64

The main fractions 2 and 3 mainly consisted of dihydroshonanic acid. Further rectifications gave a distillate with the following properties: b.p. 138.7°/6 mm.; d_4^{30} 1.009; n_D^{30} 1.4795; α_D^{24} −5.26°; M.R. obs. 47.26, calculated for $C_{10}H_{16}O_2F_1$ 47.30; Acid value 333.97, calculated for $C_{10}H_{16}O_2$ 333.3. (Found: C, 71.60; H, 9.49. Calculated for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52%. Analysis of the silver salt: Ag, 39.32. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.27%.)

Amide. The amide was prepared in white leaflets by the interaction of the acid chloride and aqueous ammonia. It was recrystallized once from 60% ethyl alcohol when it melted at 130°.

II. Oxidation of dihydroshonanic acid with potassium permanganate. 20 g. of the acid was dissolved in 600 c.c. of 1% caustic soda solution and 800 c.c. of 1.5% potassium permanganate solution was added drop by drop with vigorous stirring. After all the permanganate solution had been added, the reaction mixture was saturated in cold with carbon dioxide and then warmed on the water-bath for an hour until the permanganate has been completely consumed. The precipitate of manganese dioxide was filtered off and the filtrate was evaporated to a smaller bulk on the water-bath in an atmosphere of carbon dioxide. The solution was then slightly acidified with 5N hydrochloric acid, and the soft crystalline mass appeared was filtered and dried on a porous plate. Yield 8 g.

The crystalline substance thus separated represented dihydroxy-dihydroshonanic acid (A). A liquid acidic substance made appearance on further addition of 5N

(3) This Bulletin, **12** (1937), 253.

hydrochloric acid to the filtrate which was extracted with ether, and the ethereal solution was precipitated by the addition of light petroleum ether. The portion precipitated was separated and left to cool in an ice-box. A little dihydroxy-dihydroshonanic acid crystallized out, which was filtered off, washed with petroleum ether and dried. The viscous liquid acid obtained after the separation of the crystalline acid and evaporation of the solvent was found to consist mainly of ketonic acid of the formula $C_{10}H_{16}O_5$ (B).

Dihydroxy-dihydroshonanic acid. The crystalline acid (A) was insoluble in petroleum ether, ether and chloroform, difficultly soluble in water, but soluble in hot alcohol. The purified acid (recrystallized from hot water or alcohol) melted at 161–161.5°. The silver salt was found to dissolve readily in water. Acid value 276.22, calculated for $C_{10}H_{18}O_4$ 277.23. (Found: C, 59.09; H, 8.95. Calculated for $C_{10}H_{18}O_4$: C, 59.41; H, 8.91%.)

The liquid acid ($C_{10}H_{16}O_5$). The yield of the liquid acid (B) amounted to about 10 g. Its reactions were decidedly aldehydic. Thus it was dissolved in an excess of caustic soda solution, 5 c.c. of 30% perhydrol was added and left over night at ordinary temperature. The acid recovered from this alkaline solution was a viscous fluid with a faint reddish brown colour, which was then esterified by warming it with 30 c.c. of alcohol containing 4% hydrochloric acid.

The ethereal solution of the ester was washed with water then with 5% sodium carbonate solution successively, dried over anhydrous sodium sulphate and the ether was distilled off. The residual ester was fractionated twice under reduced pressure.

Fr. No.	B.p.	d_4^{30}	n_D^{30}	α_D^{28}	Vol. (c.c.)
1	113–116°/13 mm.	0.9738	1.4497	−6.3°	2.0
2	116–118°/13 mm.	0.9844	1.4499	−5.8°	1.0
3	118°/13 mm.–130°/3 mm.	—	—	—	1.1
4	130–140°/3 mm.	1.057	1.4583	−1.18°	3.5
5	140–150°/3 mm.	1.060	1.4563	−1.03°	2.0
6	over 150°/3 mm.	—	—	—	0.3

Judging from its physical properties as well as from its odour, fraction 1 appeared to be the ethyl ester of the unchanged dihydroshonanic acid, while the main fractions 4 and 5 were once more rectified under reduced pressure and a fraction with the following properties was obtained: b.p. 276°/758 mm.; d_4^{30} 1.059; n_D^{30} 1.4584; α_D^{28} −1.08°; M.R. obs. 70.14, calculated for $C_{11}H_{24}O_5$ 70.08; saponification value 429.3, calculated for $C_{14}H_{28}O_5$ (diethyl ester) 411.8. (Found: C, 61.85; H, 8.88. Calculated for $C_{14}H_{28}O_5$: C, 61.7; H, 8.8%.)

Application of Criegee's method on dihydroxy-dihydroshonanic acid. 10 g. of the acid was dissolved in warm benzene and 22 g. of lead tetracetate was added in small portions with vigorous stirring, filtered while hot from the precipitate and the precipitate was washed several times with ether. Then the benzene-ethereal solution was shaken with water in order to remove acetic acid liberated from lead tetracetate,

and evaporated. The viscous acid thus obtained was readily soluble in ether and alcohol but sparingly in petroleum ether. As the substance showed reactions of aldehyde its alkaline solution was treated with 5 c.c. of 30% perhydrol at 40–50°, when the reddish brown colour of the solution turned into yellow. The acid recovered as usual from this alkaline solution showed no tendency of solidification so that it was esterified by warming with 30 c.c. of alcohol containing 4% hydrochloric acid and the ester thus prepared showed the following properties: b.p. 274°/757 mm., 132–134°/2 mm.; d_4^{20} 1.054; n_D^{20} 1.4579; α_D^{20} −1.34°; saponification value 431.3, calculated for $C_{14}H_{24}O_5$ (diethyl ester) 411.8. (Found: C, 62.42; H, 8.98. Calculated for $C_{14}H_{24}O_5$: C, 61.7; H, 8.8%.)

The physical properties of the ethyl ester of the acid agreed well with those of the ester of the liquid acid $C_{10}H_{16}O_5$ (B) obtained by the oxidation of dihydroshonanic acid and was proved to be the same ketonic dicarboxylic acid by its behaviours toward oxidizing agents.

Oxidation of liquid acid $C_{10}H_{16}O_5$. The acid resulting from the saponification of the ethyl ester mentioned above was a viscous sticky substance but showed no tendency to crystallize. In order to ascertain whether the ketonic group in the molecule of the acid is an acetyl group or not, the substance was next subjected to oxidation with sodium hypochlorite, when a tricarboxylic acid should be obtained if the substance under investigation be a compound containing acetyl group.

To a solution of 4 g. of the substance dissolved in 20 c.c. of 10% sodium hydroxide solution, 8 c.c. of sodium hypochlorite solution (ca. 5.6%) was added in small portions with stirring. The reaction proceeded with evolution of heat and the smell of chloroform was perceived during the course of the reaction. After all the hypochlorite solution had been consumed the reaction mixture was refluxed for about half an hour on the water-bath, then it was evaporated to a smaller bulk and the acidic substance was recovered as usual. The ethereal solution (100 c.c.) of the acid was then stirred with 50 c.c. of water under reflux condenser at 40–50° for half an hour and the water layer separated. On evaporating the aqueous solution on the water-bath, a syrupy acid was obtained (yield 2.6 g.) which remained fluid even when kept cool for a week. The purification of the crude substance thus obtained could not be accomplished further by distillation but from the result of analysis of the silver salt and from its acid value, the substance seemed likely to represent a tribasic acid of the formula $C_9H_{14}O_6$. Acid value 744.8, calculated for $C_9H_{14}O_6$ 770.6. Analysis of the silver salt: Ag, 59.43. Calculated for $C_9H_{11}O_6Ag_3$: Ag, 60.11%. The difference between the theoretical and the experimental values may be attributed to the presence of a little unchanged acid.

Oxidation of the tricarboxylic acid $C_9H_{14}O_6$. With a view to obtain a C_8-acid, the tribasic acid obtained above was oxidized with dilute nitric acid. A mixture of 4 g. of the substance and 40 c.c. of nitric acid (d = 1.12) was warmed under reflux for 2 hours and then evaporated on the water-bath to a smaller bulk. On cooling, it deposited a little crystalline acid, which was filtered, dried on a porous plate and was purified by reprecipitation from benzene solution by the addition of light petroleum ether. Yield 0.4 g. It melted at 83° and was found to be identical with α,α-dimethylglutaric acid by melting in admixture with authentic specimen. The liquid acidic portion after removal of α,α-dimethylglutaric acid was esterified with 20 c.c. of 7% alcoholic hydrochloric acid and the ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./5mm.	d_4^{30}	n_D^{30}	Vol. (c.c.)
1	95–103°	—	1.4228	0.2
2	103–107°	0.9946	1.4286	0.6
3	107–135°	—	—	0.3
4	135–149°	1.043	1.4328	1.3

Fraction 2 was saponified as usual and after evaporating the alkaline solution on the water-bath nearly to dryness it was acidified with 2N hydrochloric acid, and the organic acid set free was extracted with ether. After removal of ether remained syrupy mass, which, on boiling with conc. hydrochloric acid for a while in a test tube and subsequent cooling, turned into a crystalline mass. The crude crystals, dried on a porous plate, melted at 74–78°, and after recrystallization from benzene melted at 82.5° and was confirmed to be identical with α,α-dimethylglutaric acid by examining the mixed melting point.

Fraction 4 was analysed without further rectification owing to the scarcity of the material. Saponification value 567.0, calculated for $C_{14}H_{24}O_6$ (triethyl ester) 583.3. (Found: C, 58.77; H, 8.49. Calculated for $C_{14}H_{24}O_6$: C, 58.33; H, 8.33%.)

The analytical data showed that the fraction consisted mainly of the triethyl ester of a tricarboxylic acid $C_8H_{12}O_6$. The free acid was regenerated from the neutral solution resulting from the determination of the saponification value. The solution was evaporated nearly to dryness on the water-bath and was acidified with hydrochloric acid and the free organic acid liberated was extracted with chloroform, dried over anhydrous sodium sulphate, and evaporated. The residue showed no tendency to crystallize even when kept ice-cold for several days. Then it was gently heated with conc. hydrochloric acid for about half an hour under reflux as in the previous case. On cooling, a minute quantity of crystals made appearance, so that the heating was continued for further 3 hours and kept cool over night in an ice-box. The crystalline acid thus deposited was filtered, and dried on a porous plate. It melted at 87° when purified by reprecipitation from chloroform solution by the addition of light petroleum ether and proved to be identical with α,α-dimethylglutaric acid. Thus it should be concluded that the free tricarboxylic acid has transformed into α,α-dimethylglutaric acid by elimination of one mol of carbon dioxide therefrom.(4)

III. Ozonolysis of dihydroshonanic acid. A well-cooled solution of 10 g. of the acid in 100 c.c. of carbon tetrachloride was treated with ozonized oxygen (containing ca. 5% ozone) at a rate of 20–25 l. per hour. The ozonide formed was crystalline and remained suspended in the solution. It was filtered, washed with carbon tetrachloride, heated to gentle boiling with 100 c.c. of 3.5% solution of sodium carbonate, and then a calculated quantity of 3% perhydrol was added drop by drop with constant stirring in order to oxidize the aldehyde group into the carboxyl, meanwhile sodium carbonate solution being added little by little to maintain the reaction mixture

(4) Analogous with the case of preparation of α,α-dimethylsuccinic acid [Leukart, *Ber.*, **18** (1885), 2550] or α,α-dimethyladipic acid [Blanc, *Bull. soc. chim.*, [4], **3** (1890), 288] from isobutane-α,α,β-tricarboxylic acid or α,α-dimethyl-α′-carboxy-adipic acid respectively.

slightly alkaline. The acidic substance recovered (amounted to ca. 9 g.) from the reaction mixture was a viscous substance with a light reddish brown colour and showed positive reaction toward Schiff's reagent and Tollens' solution. As the substance remained liquid even when kept cold for several days, it was directly oxidized by heating it with dilute nitric acid (d = 1.12) on the water-bath for 2 hours, evaporated, and esterified by warming with 50 c.c. of ethyl alcohol containing 4% hydrochloric acid. The ester formed was fractionally distilled under reduced pressure.

Fr. No.	B.p./2mm.	d_4^{21}	n_D^{21}	α_D^{21}	Wt.(g.)
1	78–135°	0.9722	1.4614	−0.8°	1.8
2	135–140°	1.082	1.4570	−0.3°	5.2

Fraction 2 was once more rectified and the portion 138–140°/6 mm. was collected, which showed the following properties: d_4^{29} 1.083; n_D^{29} 1.4535; α_D nil; M.R. obs. 60.96, calculated for $C_{12}H_{20}O_5$ 60.88; saponification value 474.5, calculated for $C_{12}H_{20}O_5$ (diethyl ester) 459.0. (Found: C, 59.13; H, 8.41. Calculated for $C_{12}H_{20}O_5$: C, 59.0; H, 8.2%.)

Preparation of the semicarbazone. The ester gave a crystalline semicarbazone melting at ca. 149° without any purification, which when purified by one recrystallization from 60% alcohol melted at 154–156°. The further purification from the same solvent was impossible. (Found: N, 14.26. Calculated for $C_{13}H_{23}O_5N_3$: N, 13.95%.)

Preparation of α,α-dimethylglutaric acid from ketonic diethyl ester $C_{12}H_{20}O_5$. 3 g. of the viscous liquid acid obtained by saponification of the diethyl ester mentioned above was dissolved in 60 c.c. of caustic soda solution, to which 40 c.c. of 30% perhydrol was added with constant stirring at 40–50°. When the peculiar reddish brown colour of the solution disappeared, the reaction mixture was evaporated on the water-bath, acidified with dilute hydrochloric acid and organic acid set free was extracted with chloroform. On removal of chloroform there remained a yellowish sticky substance, which turned into a crystalline mass on warming with conc. hydrochloric acid as in the previous cases. The crystalline acid was also identical with α,α-dimethylglutaric acid.

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Measurement of Circular Dichroism in the Ultra-Violet Regions. I.

By Ryutaro TSUCHIDA.

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Introduction. A method of measuring circular dichroism in the ultra-violet as well as the visible regions was devised by Kuhn and Braun.[1] The general principle of the method is as follows. By means of a half-shadow polarizer of a split prism and a Fresnel rhomb set parallel to the polarizer, two elliptically polarized rays of opposite sign and of equal ellipticity are produced. On traversing d cm. of a c mol/l. solution of an optically active compound whose molar extinction coefficients for left and right circular vibrations are ε_l and ε_r, the two rays will have their ellipticities changed. By rotating the polarizer, the ellipticities of the rays incident on the solution can be made unequal until those of the emergent rays are again equal. This is tested by an analyser placed so as to transmit only those vibrations corresponding to the minor axes of the two ellipses. Let τ be the angle through which the polarizer has been rotated to obtain an equal brightness after passing through the optical system, then the difference between the molar extinction coefficients is given by the following relation

$$\varepsilon_l - \varepsilon_r = \frac{4\tau}{cd} . \qquad (1)$$

In deriving the relation, however, the following limitations have been introduced. Let θ be half the angle between the two vibration directions of the polarizer. The values of θ and τ should be so small as to satisfy the relations, $\tan\theta \simeq \theta$, $\tan(\theta+\tau) \simeq \theta+\tau$ and $\tan(\theta-\tau) \simeq \theta-\tau$, and α, the rotation caused by the active compound, should also be very small. Besides these limitations, some more approximate calculations have been introduced in course of derivation of the relation (1), and consequently it seems insufficient for further discussions. The present author has derived a general equation for circular dichroism measurements in which both the polarizer and the analyser are rotated and all

(1) Kuhn and Braun, *Z. physik. Chem.*, B, **8** (1930), 445.

the above-mentioned limitations have been abolished. By means of the equation, experimental conditions have been discussed.

Derivation of the Equation. Let 2θ be the angle between the vibration directions of prisms P_1 and P_2 of the half-shadow polarizer and τ, the angle between the bisectrix of the two planes of vibration of P and the Fresnel rhomb F, whose vibration directions are taken as co-ordinate axes throughout the calculation. Then the plane polarized rays produced by the prisms P_1 and P_2 contain $\tau+\theta$ and $\tau-\theta$ respectively with the x-axis. The intensity of the two rays after passing through the polarizer being equal, the amplitude is denoted by a_0. Then the two rays may be expressed by

$$a = a_0 \cos 2\pi\nu t .$$

On entering the Fresnel rhomb each of these rays is split into two components, one propagating in a plane parallel to the rhomb and the other perpendicular. The amplitudes of these components, a_x and a_y, are

$$\left.\begin{aligned}(a_x)_1 &= a_0 \,|\cos(\tau+\theta)\,| \\ (a_y)_1 &= a_0 \,|\sin(\tau+\theta)\,|\end{aligned}\right\} \text{ for } P_1 ,$$

and

$$\left.\begin{aligned}(a_x)_2 &= a_0 \,|\cos(\tau-\theta)\,| \\ (a_y)_2 &= a_0 \,|\sin(\tau-\theta)\,|\end{aligned}\right\} \text{ for } P_2 .$$

The light waves before the first total reflexion in the rhomb are

$$\left.\begin{aligned}x_1 &= a_0 \cos(\tau+\theta)\cos 2\pi\nu t \\ y_1 &= a_0 \sin(\tau+\theta)\cos 2\pi\nu t\end{aligned}\right\} \text{ for } P_1 ,$$

and

$$\left.\begin{aligned}x_2 &= a_0 \cos(\tau-\theta)\cos 2\pi\nu t \\ y_2 &= a_0 \sin(\tau-\theta)\cos 2\pi\nu t\end{aligned}\right\} \text{ for } P_2 .$$

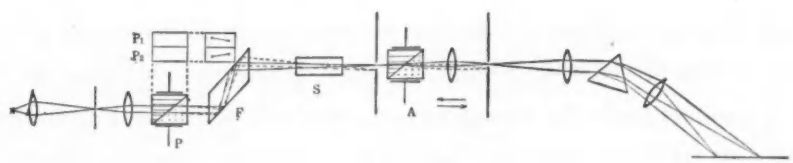

Fig. 1.

After the second total reflexion in the rhomb, each of these two pairs of plane polarized rays receives a phase difference of $\frac{\pi}{2}$, and the waves become

$$\left.\begin{aligned} x_1 &= a_0 \cos(\tau+\theta)\cos 2\pi\nu t \\ y_1 &= a_0 \sin(\tau+\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{ for } P_1,$$

and

$$\left.\begin{aligned} x_2 &= a_0 \cos(\tau-\theta)\cos 2\pi\nu t \\ y_2 &= a_0 \sin(\tau-\theta)\sin 2\pi\nu t \end{aligned}\right\} \text{ for } P_2.$$

The resultant vibration for P_1 and P_2 after passing through the rhomb may, therefore, be expressed as

$$\left.\begin{aligned} \mathbf{R}_1 &= \mathbf{i}a_0 \cos(\tau+\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau+\theta)\sin 2\pi\nu t \\ \text{and}\quad \mathbf{R}_2 &= \mathbf{i}a_0 \cos(\tau-\theta)\cos 2\pi\nu t + \mathbf{j}a_0 \sin(\tau-\theta)\sin 2\pi\nu t. \end{aligned}\right\} \quad (2)$$

These expressions represent elliptically polarized lights whose sense of rotation depends on τ and θ. The elliptically polarized ray is lævorotatory when P_1 is in the first and the third quadrant, and dextrorotatory otherwise. The same holds for P_2.

First the intensity of the elliptically polarized lights is compared directly with the analyser A. Let the angle between the analyser and the Fresnel rhomb be δ_0, at which the two fields of the half-shadow are of equal brightness, then

$$a_0^2 \cos^2(\tau+\theta)\cos^2\delta_0 + a_0^2 \sin^2(\tau+\theta)\sin^2\delta_0 = a_0^2 \cos^2(\tau-\theta)\cos^2\delta_0 + a_0 \sin^2(\tau-\theta)\sin^2\delta_0.$$

Solving this equation we obtain

$$\tan\delta_0 = \pm 1. \qquad \therefore\ \delta_0 = \frac{\pi}{4}(1\pm 2n).$$

Then δ_0 is independent of τ and θ; in other words the two fields of the half-shadow are of equal brightness when the analyser is placed at $\frac{\pi}{4}$ or $\frac{3}{4}\pi$ referring to the Fresnel rhomb, whatever the angle between the polarizer and the rhomb and that between the two vibration directions of the half-shadow polarizer may be. This relation gives us the means

of determining the relative angular position of the analyser referred to the Fresnel rhomb and consequently the zero point of the measurement.

Next let us consider the case when a solution of active substance is introduced between the Fresnel rhomb and the analyser. As the active substance has different extinction coefficients for left and right circularly polarized vibrations, each of the elliptically polarized rays represented by the equations (2) should first be transformed as a resultant of circularly polarized waves of opposite rotatory sense.

Thus
$$\mathbf{R}_1 = \frac{a_0}{2}\{\cos(\tau+\theta)+\sin(\tau+\theta)\}(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{2}\{\cos(\tau+\theta)-\sin(\tau+\theta)\}(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t),$$

or
$$\left.\begin{aligned}\mathbf{R}_1 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\ &+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t).\end{aligned}\right\}$$

And similarly
$$\left.\begin{aligned}\mathbf{R}_2 &= \frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}+\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)\\ &+\frac{a_0}{\sqrt{2}}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t).\end{aligned}\right\} \qquad (2)'$$

In each of these equations the first and the second term represents a circularly polarized ray whose sense of rotation is anticlockwise and clockwise respectively.

After traversing the solution S, the vibrations are changed as follows. follows.

$$\mathbf{R}_1' = \frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t+\mathbf{j}\sin 2\pi\nu t)$$
$$+\frac{a_0}{\sqrt{2}}e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\cdot(\mathbf{i}\cos 2\pi\nu t-\mathbf{j}\sin 2\pi\nu t),$$

or
$$\mathbf{R}_1' = \mathbf{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathrm{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}\sin 2\pi\nu t\,. \tag{3}$$

$$\mathbf{R}_2'=\mathrm{i}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\cos 2\pi\nu t$$

$$+\mathrm{j}\frac{a_0}{\sqrt{2}}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}\sin 2\pi\nu t\,. \tag{4}$$

Both the expressions (3) and (4) represent elliptically polarized rays.

The intensity of the two half-shadow fields observed through the analyser A, which is placed at an angle ω to the common axis of the elliptically polarized rays, (3) and (4), corresponding to the x-axis of the co-ordinates, is given by the following expressions.

$$I_1=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau+\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau-\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau+\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau-\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau+\theta)\cos 2\omega\right\}. \tag{5}$$

$$I_2=\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\cos^2\omega$$

$$+\frac{a_0^2}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd}\sin\left(\frac{\pi}{4}+\tau-\theta\right)-e^{-\frac{1}{2}\varepsilon_r cd}\sin\left(\frac{\pi}{4}-\tau+\theta\right)\right\}^2\sin^2\omega$$

$$=\frac{a_0^2}{2}\left\{e^{-\varepsilon_l cd}\sin^2\left(\frac{\pi}{4}+\tau-\theta\right)+e^{-\varepsilon_r cd}\sin^2\left(\frac{\pi}{4}-\tau+\theta\right)\right.$$

$$\left.+e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2(\tau-\theta)\cos 2\omega\right\}. \tag{6}$$

$$\therefore\quad I_1-I_2=\frac{a_0^2}{2}\sin 2\theta\left\{\left(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\right)\cos 2\tau-2e^{-(\varepsilon_l+\varepsilon_r)cd}\sin 2\tau\cos 2\omega\right), \tag{7}$$

$$\text{and} \quad I_1+I_2=\frac{a_0^2}{2}\Big\{e^{-\varepsilon_l cd}+e^{-\varepsilon_r cd}+\left(e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}\right)\cos 2\theta \sin 2\tau$$

$$+2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2\theta \cos 2\tau \cos 2\omega\Big\}. \qquad (8)$$

When the two half-shadow fields are of equal brightness, the expression (7) must be zero. As $\sin 2\theta$ can not be zero, we obtain

$$e^{-\varepsilon_l cd}-e^{-\varepsilon_r cd}=2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\tan 2\tau \cos 2\omega . \qquad (9)$$

$$\therefore \quad e^{\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}-e^{-\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd}=2\tan 2\tau \cos 2\omega ,$$

or
$$\sinh\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd=\tan 2\tau \cos 2\omega . \qquad (9)'$$

$$\therefore \quad \varepsilon_r-\varepsilon_l=\frac{2}{cd}\operatorname{arcsinh}(\tan 2\tau \cos 2\omega) . \qquad (10)$$

Now τ is the angle between the polarizer and the Fresnel rhomb, and ω is given by $\omega=\delta-\alpha$, where δ is the angle between the Fresnel rhomb and the analyser and α is the angle of rotation. By measuring these angles, the circular dichroism can be calculated by the relation (10).

Approximate Equations. As we have introduced neither limitation nor approximation of any kind in course of calculation, the relation (10) holds for any values of θ, ω, and τ, as well as for any values of c and d, provided that the two fields observed through the analyser are of equal brightness.

In special cases when $\frac{1}{2}(\varepsilon_r-\varepsilon_l)cd$ is small,

$$\varepsilon_e-\varepsilon_l\simeq\frac{2}{cd}\tan 2\tau \cos 2\omega . \qquad (11)$$

Moreover, when ω is $\frac{\pi}{2}$ and τ is very small, we obtain an approximate equation,

$$\varepsilon_l-\varepsilon_r\simeq\frac{4\tau}{cd} \qquad (1)$$

which is identical with that of Kuhn and Braun referred to in the introduction. In other words the Kuhn's equation is one of the most special cases of our equation (10).

Calculation of the error caused by applying the approximate equation (1) is complicated and very difficult, as there are too many approximations and neglections as to τ and $(\varepsilon_r - \varepsilon_l)cd$ as well as α which is again a function of c and d. Consequently it is impossible to find the range of applicability of the approximate equation (1).

On the other hand, however, it may be easily determined for the approximate equation (11) how far it could be applied without causing serious error in the results of the measurement. The calculation is as follows. From the relation (10)

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\mathrm{d}c}{c} - \frac{\mathrm{d}d}{d} + \frac{\mathrm{d}(\tan 2\tau \cos 2\omega)}{\sqrt{1+\tan^2 2\tau \cos^2 2\omega}\ \operatorname{arcsinh}(\tan 2\tau \cos 2\omega)} . \quad (12)$$

$$\operatorname{arcsinh}(\tan 2\tau \cos 2\omega) = \frac{1}{2}(\varepsilon_r-\varepsilon_l)cd \equiv x \quad \text{(put)}. \quad (10)'$$

Then

$$\tan 2\tau \cos 2\omega = \sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \frac{x^7}{7!} + \cdots . \quad (9)''$$

Now the approximate equation (11) may be rewritten as

$$\tan 2\tau \cos 2\omega \simeq x. \quad (11)'$$

Thus the error caused by using the approximate equation (11) is given by comparing (9)″ and (11)′

$$\mathrm{d}(\tan 2\tau \cos 2\omega) = -\left\{\frac{x^3}{3!} + \frac{x^5}{5!} + \cdots\right\} . \quad (13)$$

Substituing (9)″ and (13) in (12), we obtain

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\mathrm{d}c}{c} - \frac{\mathrm{d}d}{d} - \frac{\frac{x^2}{3!} + \frac{x^4}{5!} + \cdots}{\sqrt{1+\tan^2 2\tau \cos^2 2\omega}} .$$

As the first and the second term has nothing to do with the approximate equation,

$$\frac{\mathrm{d}(\varepsilon_r-\varepsilon_l)}{\varepsilon_r-\varepsilon_l} = -\frac{\frac{x^2}{3!} + \frac{x^4}{5!} + \cdots}{\sqrt{1+\tan^2 2\tau \cos^2 2\omega}} . \quad (12)'$$

Therefore the value of x which would provoke an error of 1% in $(\varepsilon_r - \varepsilon_l)$ may be computed as follows.

$$-\frac{1}{100} = -\frac{\frac{x^2}{3!}+\frac{x^4}{5!}+\cdots}{\sqrt{1+\tan^2 2\tau\cos^2 2\omega}}.$$

When x is a small fraction

$$\frac{x^4}{5!}+\frac{x^2}{3!} = \frac{1}{100}\sqrt{1+x^2}\ .$$

Solving the equation, we obtain

$$x = \pm 0.253.$$

In order to make use of the approximate equation (11) with a permissible error less than 1%, the following condition should be complied with.

$$|(\varepsilon_r-\varepsilon_l)|\,cd < 0.50.$$

Similarly for a permissible error less than 0.1

$$|(\varepsilon_r-\varepsilon_l)|\,cd < 0.15.$$

and for 0.01

$$|(\varepsilon_r-\varepsilon_l)|\,cd < 0.04.$$

Circular Dichroism of Ammonium α-Bromocamphor-π-Sulphonate. The molar extinction coefficient κ (as in $I = I_0 \times 10^{\kappa cd}$) and the specific rotation $[\alpha]$ of the salt were measured with 0.01 mol/l. aqueous solutions with thicknesses between 0.3 and 4 cm. The circular dichroism $\kappa_r - \kappa_l$, i.e., $0.434 \times (\varepsilon_r - \varepsilon_l)$ was determined according to the method described above. The strength of the solution was 0.01 mol/l. and the thickness of the layer was 1 cm. throughout the measurements. The results are shown in Fig. 2.

The author wishes to express his sincere thanks to Professor Y. Shibata for his kind advice and encouragement and also to the Hattori Hôkôkai for a grant. In addition the author should like to record his gratitude to Mr. M. Kobayashi and Mr. H. Watanabe for their helpful assistance.

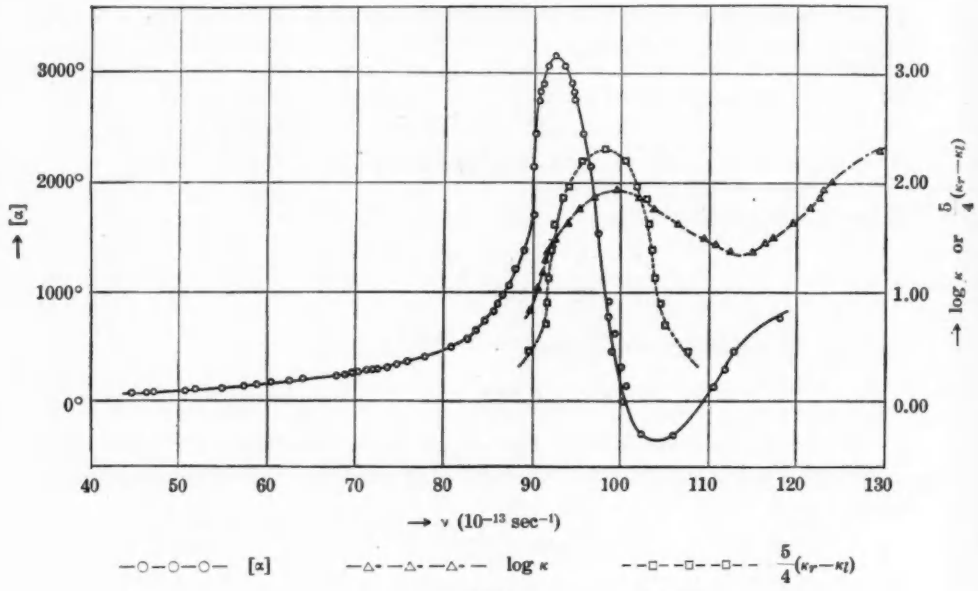

Fig. 2.

Summary.

1. An accurate method of measuring circular dichroism has been proposed.

2. The general equation for the measurement has been worked out.

$$\varepsilon_r-\varepsilon_l=\frac{2}{cd}\,\mathrm{arcsinh}\,(\tan 2\tau\cos 2\omega)\ .$$

3. The range of applicability was discussed for the approximate equation,

$$\varepsilon_r-\varepsilon_l=\frac{2}{cd}\tan 2\tau\cos 2\omega\ .$$

In order to make use of this equation with permissible errors less than 0.01, 0.1, and 1%, the following conditions should be complied with:

$$|(\varepsilon_r-\varepsilon_l)cd|<0.04 \qquad \text{for} \quad 0.01\%\ ,$$

$$|(\varepsilon_r-\varepsilon_l)cd| < 0.15 \quad \text{for} \quad 0.1\ \%\ ,$$

and $$|(\varepsilon_r-\varepsilon_l)cd| < 0.50 \quad \text{for} \quad 1\ \%\ .$$

4. The light absorption, the rotatory dispersion, and the circular dichroism in the visible and the ultra-violet regions were measured for ammonium α-bromocamphor-π-sulphonate.

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Studies on the Flow of Gaseous Mixtures through Capillaries. II. The Molecular Flow of Gaseous Mixtures.

By Hiroshi ADZUMI.

(Received May 26th, 1937.)

In the preceding paper[1] on the flow of gaseous mixtures, the author dealt with the case where the mean free path of the gas molecule of each component is small in comparison with the diameter of the capillary. When the mean free path is large in comparison with the diameter, the number of mutual collisions between gas molecules is negligible as compared with that of collisions with the wall. In such a case, Knudsen[2] has assumed "the diffuse emission" from the wall of the capillary, namely, the molecules in the capillary leave a surface uniformly in all directions regardless of the directional distribution with which they hit the surface and are governed by the cosine law. As a result of this behaviour some of the molecules entering the mouth of the capillary are reversed and sent back to the vessel from which they came. Hence the number of molecules flowing through the capillary is a certain fraction of the total number of entering molecules and this fraction is determined only by the number of collisions with the wall of the capillary and not by the collisions between molecules.

(1) H. Adzumi, this Bulletin, **12** (1937), 199.
(2) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.

When the mean free path is large against the diameter of the capillary, the quantity of a simple gas flowing through the capillary in unit time is given by Knudsen as follows:

$$G_m = b(p_1 - p_2) , \tag{1}$$

where

$$b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{r^3}{l} ,$$

ρ_1 is the density of the gas at the temperature of the capillary and at unit pressure (1 dyne/cm.^{2}), l and r are the length and the radius of the capillary respectively, p_1 and p_2 the pressures at the ends of the capillary, and G_m is measured by the product of its volume and pressure. Thus the amount of gas flowing per unit time is independent of the viscosity but inversely proportional to the square root of the molecular weight and therefore such a flow is called the molecular flow.

In their theoretical considerations of the flow of gases Maxwell[3], Smoluchowski[4], Gaede[5], and Baule[6] made the assumption that only a fraction f of the impinging molecules leave the wall according to the cosine law and that the reflection for remaining 1-f are specular. However, from the experiments, Knudsen gave the value of f as unity.

In an ideal gaseous mixture, each component is completely independent of the other, since the molecules do not affect each other within the capillary. Therefore the amount of flow of a mixture will be strictly additive or

$$b = n_1 b_1 + n_2 b_2 , \tag{2}$$

where n_1 and n_2 are mol fractions of two components.

In order to examine this point the following experiments have been done.

Experimental.

Apparatus for Measuring the Quantity of Flow. Fig. 1 is a schematic view of the apparatus. Glass bulbs A and B, both about 1 liter in capacity, are connected with the capillary C, whose radius is ca. 0.0121 cm. and length 8.7 cm. The pressure of each bulb is read by the McLeod gauge which is constructed to be able to measure from 10^{-5} to 10 mm. D and E are mercury cut-offs. When the mercury is raised to

(3) J. Maxwell, *Trans. Roy. Soc.* (London), A, **170** (1879), 251.
(4) M. v. Smoluchowski, *Ann. Physik*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*, (IV), **41** (1913), 289.
(6) B. Baule, *ibid.*, (IV), **44** (1914), 145.

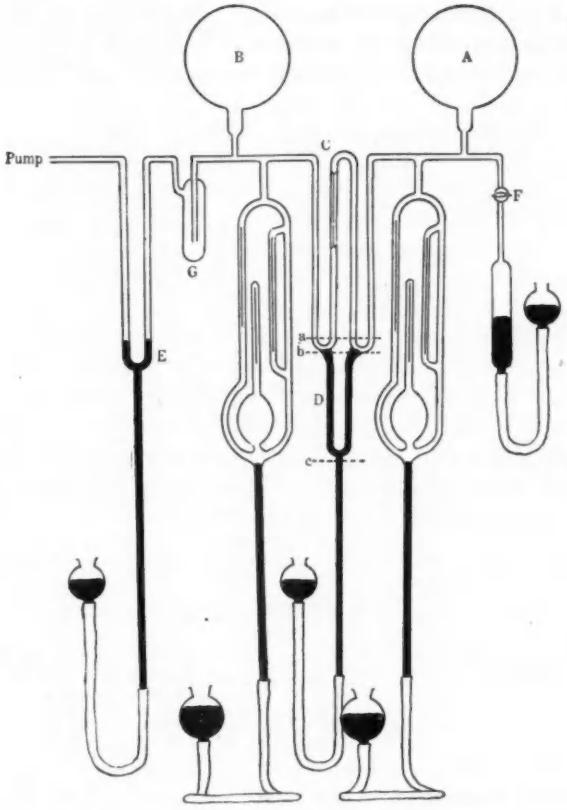

Fig. 1.

c, two bulbs are connected without the capillary, when raised to b, the gas flows through the capillary, and when raised to a, the flow is cut off.

After evacuation of the whole apparatus and raising the mercury to a, the required quantity of the gas is introduced into A from F. Then, by lowering the mercury to b, the gas in A begins to flow through the capillary, the volume on each side being kept constant.

If V_1 and p_1 represent the volume and the pressure of the right side of the capillary and V_2 and p_2 those of the left side, the quantity of gas flowing in time $d\tau$ through the capillary is expressed as

$$Q \cdot d\tau = K(p_1 - p_2)\, d\tau = -d(p_1 V_1) = d(p_2 V_2)\,,$$

where K is a proportionality constant or the quantity of flow under unit pressure difference, $-d(p_1V_1)$ a quantity decreased in the right side of the capillary, and $d(p_2V_2)$ a quantity increased in the left side.
Then,

$$\frac{K\cdot d\tau}{V_1} = -\frac{dp_1}{p_1-p_2} \quad \text{and} \quad \frac{K\cdot d\tau}{V_2} = \frac{dp_2}{p_1-p_2},$$

From these formulæ,

$$\frac{d(p_1-p_2)}{p_1-p_2} = -K\left(\frac{1}{V_1}+\frac{1}{V_2}\right)d\tau .$$

By integration

$$K = -\frac{\ln\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau}\,\frac{V_1\,V_2}{V_1+V_2},$$

where p_1' and p_2' are the pressures of bulbs after time $d\tau$. The values of V_1 and V_2 are 1371 c.c. and 1406 c.c. respectively, so that K is calculated by the following formula:

$$K = -\frac{\log\dfrac{p_1'-p_2'}{p_1-p_2}}{\tau}\times 1.856\times 10^3 \text{ (in mm.} \times \text{c.c.).}$$

The mean pressure of both ends of the capillary is calculated by

$$p = \frac{p_1V_1+p_2V_2}{V_1+V_2}.$$

Results of Observation. The gaseous mixtures used for observation are $H_2\sim C_2H_2$ and $H_2\sim C_3H_6$. The preparation of these gases was described in the preceding paper.[1] The measuring temperature was $20+0.5°C$. The pressure range was between 4 and 10^{-3}mm. The time of flow was 2–4 hours.

Generally the values of K are a function of the mean pressure p, but become a constant when p is so small that the mean free path of the gas is large against the diameter of the capillary. This constant value corresponds to the rate of the molecular flow, b. When the pressures of hydrogen, acetylene, and propylene are lower than 0.06 mm., 0.03 mm., and 0.03 mm. respectively, the values of K become constants, which are 0.0750 for H_2, 0.0220 for C_2H_2, and 0.0164 for C_3H_6.

The values of K at the pressures higher than those will be reported in the following paper.

Table 1. The Rates of the Molecular Flow of Simple Gases.

Gas	b (mm.×c.c.)	
	obs.	calc.
H_2	0.0750	0.0750
C_2H_2	0.0220	0.0208
C_3H_6	0.0164	0.0161

The rates of the molecular flow, b, of three simple gases can be calculated by equation (1), by inserting the following values: $l = 8.7$ cm., $r = 0.0121$ cm.; ρ_1 at 20°C. of $H_2 = 8.266 \times 10^{-11}$, $C_2H_2 = 107.88 \times 10^{-11}$, $C_3H_6 = 172.21 \times 10^{-11}$. These calculated values of b agree very well with the observed values of K at very low pressures. (Table 1.) This agreement shows that the fraction f of the molecules which leave the wall according to the cosine law is unity.

The values of K of a mixture, similarly as a simple gas, become a constant at very low pressures. In the cases of the flow of mixtures at low pressures, the compositions change every moment, since the quantities were measured at every thirty minutes and the quantities of flow of the initial compositions were obtained by extrapolating to time zero.

The values of b of mixtures are given in Table 2.

Table 2. The Rates of the Molecular Flow of Mixtures.

$H_2 \sim C_2H_2$

H_2%	C_2H_2%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.69	24.31	0.0622	0.0621
51.18	48.82	0.0490	0.0491
25.97	74.03	0.0354	0.0358
0.00	100.00	0.0220	0.0220

$H_2 \sim C_3H_6$

H_2%	C_3H_6%	b (mm.×c.c.)	
		obs.	calc.
100.00	0.00	0.0750	0.0750
75.18	24.82	0.0610	0.0604
50.82	49.18	0.0458	0.0462
0.00	100.00	0.0164	0.0164

In Table 2, the values of b given in the fourth column are calculated by formula (2).

As seen from Table 2, the rates of molecular flow of gaseous mixtures strictly follows the additivity law.

The Separation of Mixtures caused by Flowing through Capillaries at Low Pressures. At very low pressures, each component of a mixture flows independently of the other, namely the separation of a mixture into components takes place. Consequently, by measuring the separation of the mixtures after flow, the additivity of the flowing quantity of mixtures may be confirmed.

In order to know the separation of the mixture $H_2 \sim C_2H_2$, the quantities of acetylene after flow were analysed by the following method: The trap G in Fig. 1 was cooled with liquid air and hydrogen was removed by vacuum pump, acetylene being condensed to solid state in G. Then acetylene in the trap was vaporised by removing the liquid air and its pressure was read. If the total pressure before the application of liquid air is known, the composition of the mixture after flow can be calculated. This analytical method has been examined beforehand by analysing the mixtures of known compositions and has been found that it can be used to know the composition within the experimental error of a few per cent.

The changes of the compositions of the mixtures after flowing through the capillary for two hours are given in Table 3.

Table 3. The Change of the Compositions after Flowing through the Capillary. (Fig. 2.)

Mixture I. (H_2: 51.18%, C_2H_2: 48.82%)			Mixture II. (H_2: 75.69%, C_2H_2: 24.31%)		
$p_{mm.}$	H_2%	C_2H_2%	$p_{mm.}$	H_2%	C_2H_2%
3.161	51.0	49.0	2.780	75.7	24.3
2.064	51.2	48.8	1.914	75.6	24.4
0.828	54.0	46.0	1.204	75.7	24.3
0.518	59.6	40.4	0.725	79.0	21.0
0.200	69.0	31.0	0.475	81.9	18.1
0.1471	72.0	28.0	0.273	85.8	14.2
0.0659	76.0	24.0	0.1453	88.0	12.0
0.0493	75.8	24.2	0.0581	89.5	10.5

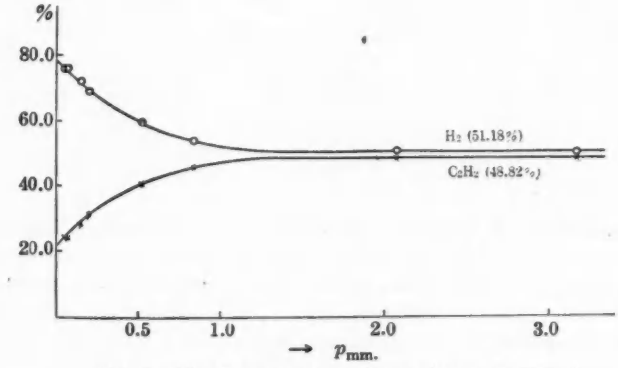

Fig. 2. The Change of the Compositions of Mix. I.

As seen from Fig. 2, the mixtures flow without separation at the pressures higher than about 1 mm. but at the pressures lower than this the separation takes place. By extrapolation of the curves to $p = 0$, the hydrogen percentages of the mixtures after flow at very low pressures can be obtained. These values are 78.5% for mixture I and 91.0% for mixture II and agree very well with the values which are calculated by considering that the component flows independently of the other. (Table 4.)

Table 4. The Hydrogen Percentages of the Mixtures after Flow at Very Low Pressures.

	H_2%	
	obs.	calc.
Mixture I	78.5	78.1
„ II	91.0	91.5

The same analytical method was applied to the mixture of hydrogen and propylene, but as the latter does not condense to solid state, there is an appreciable loss during the evacuation. Hence the reading of the pressure of propylene after evaporation was not accurate enough to compute the exact concentration.

Summary.

(1) The quantities of the following simple gases and gaseous mixtures flowing through the capillary at very low pressures have been measured.

$$H_2,\ C_2H_2,\ C_3H_6,\ H_2 \sim C_2H_2,\ H_2 \sim C_3H_6.$$

(2) The rates of the molecular flow of simple gases are expressed satisfactorily by Knudsen's formula.

(3) The rates of the molecular flow of mixtures are considered to be additive of the components. This consideration has been confirmed by the measurements of the quantities of flow of mixtures.

(4) The changes of the compositions of the mixtures after flowing through the capillary at low pressures have been measured and the results show also the validity of the additivity law.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

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Studies on the Flow of Gaseous Mixtures through Capillaries. III. The Flow of Gaseous Mixtures at Medium Pressures.

By Hiroshi ADZUMI.

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In the previous papers[1][2], the author reported the studies on the flow of gaseous mixtures when the mean free paths of molecules are small or large in comparison with the diameter of the capillary. When the mean free path is small against the diameter, the quantity of a gas flowing in unit time is expressed by the following formula:

$$G_v = ap(p_1 - p_2), \tag{1}$$

where

$$a = \frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l},$$

η is the viscosity of the gas, p_1 and p_2 the pressures at the ends of the capillary, p the mean of these, and l and r are the length and the radius of the capillary. When the mean free path is large against the diameter, the quantity is expressed by

$$G_m = b(p_1 - p_2), \tag{2}$$

where

$$b = \frac{4}{3}\sqrt{2\pi}\frac{1}{\sqrt{\rho_1}}\frac{r^3}{l},$$

ρ_1 is the density of the gas at unit pressure.

At medium pressures when the mean free path is comparable with the diameter, two above formulæ overlap each other and we may set as follows:

$$Q = G_v + \gamma G_m = K(p_1 - p_2),$$

or

$$K = ap + \gamma b, \tag{3}$$

where γ is a coefficient which is equal to or smaller than unity.

In order to examine formula (3) for simple gases and binary gaseous mixtures, the following experiments have been done.

The Quantities of Flow of Simple Gases. The procedure for measuring the quantity of flow is the same as already described.[2] The quanti-

(1) This Bulletin, **12** (1937), 199.
(2) *Ibid.*, **12** (1937), 285.

ties of hydrogen, acetylene, and propylene flowing in unit time and under unit pressure difference are given in Table 1. The mean pressures are measured in mm. In such a case, the formula of the quantity of flow becomes

$$K = \frac{\pi}{8}\frac{1}{\eta}\frac{r^4}{l}\frac{1013250}{760}p+\gamma\times 3.05\times 10^4\sqrt{\frac{T}{M}}\frac{r^3}{l}$$

$$= 5.236\times 10^2\frac{1}{\eta}\frac{r^4}{l}p+\gamma\times 3.05\times 10^4\sqrt{\frac{T}{M}}\frac{r^3}{l}, \qquad (4)$$

where M is the molecular weight of the gas and T the absolute temperature.

In Fig. 1, K is shown as function of the mean pressure. As seen from the figure, the observed values of K decrease with the decrease of the pressure, lying on a straight line at higher pressures, then after passing through a minimum, become a constant at very low pressures. As described in the preceding paper, this constant corresponds to the rate of the molecular flow. The shape of the curves in Fig. 1 shows that the flow can be expressed by formula (3).

The gradient a can be obtained from the straight part and by using it we can calculate the values of γ, which is shown in the fourth column

Table 1. The Quantities of Flow of Simple Gases. (Fig. 1.)

Hydrogen. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.811	0.1075	0.0680	0.91	
1.869	0.0939	0.0677	0.90	
1.269	0.0858	0.0680	0.91	
0.893	0.0814	0.0689	0.92	0.91
0.634	0.0769	0.0680	0.91	
0.526	0.0744	0.0670	0.89	
0.443	0.0742	0.0680	0.91	
0.1841	0.0730	0.0704	0.94	
0.0606	0.0745	0.0737	0.98	
0.0438	0.0746	0.0740	0.99	
0.0382	0.0748	0.0743	0.99	
0.0211	0.0750	0.0747	1.00	
0.0137	0.0750	0.0748	1.00	

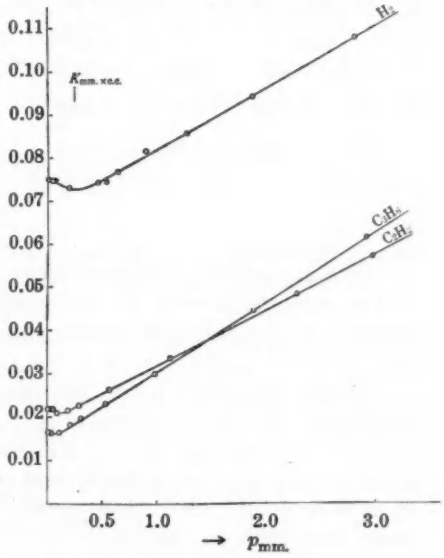


Fig. 1.

Acetylene. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.993	0.0575	0.0195	0.89	
2.284	0.0485	0.0195	0.89	
1.125	0.0336	0.0193	0.88	0.88
0.564	0.0264	0.0192	0.87	
0.287	0.0226	0.0190	0.86	
0.1824	0.0215	0.0192	0.87	
0.0913	0.0210	0.0198	0.90	
0·0453	0.0218	0.0212	0.96	
0.0239	0.0222	0.0219	1.00	
0.0119	0.0220	0.0218	0.99	
0.0066	0.0220	0.0219	1.00	

Propylene. (20°C.)

$p_{mm.}$	K	$K-ap$	γ	
2.940	0.0616	0.0149	0.91	
1.894	0.0448	0.0148	0.90	
0.984	0.0302	0.0147	0.90	
0.531	0.0232	0.0148	0.90	0.90
0.303	0.0197	0·0149	0.91	
0.213	0.0183	0.0149	0.91	
0.1050	0.0165	0.0148	0.90	
0.0585	0.0162	0.0153	0.93	
0.0353	0·0164	0.0158	0.96	
0.0243	0.0164	0.0160	0.98	
0.0102	0.0164	0.0162	0.99	

of Table 1. The observed values of a agree very well with the values calculated from the viscosities and this comparison is shown in Table 2.

Table 2.

	$\eta_{20°} \times 10^7$	a	
		obs.	calc.
H_2	924	0.0141	0.0141
C_2H_2	1022	0.0127	0.0127
C_3H_6	848	0.0159	0.0153

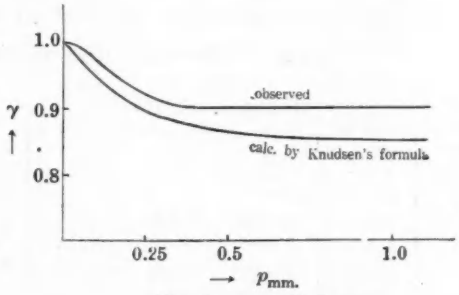


Fig. 2. γ of Hydrogen

The coefficient γ of simple gas is a function of the mean pressure and is constant at very low pressures, where it is equal to 1.0, and also constant at the pressures higher than about 0.4 mm., where it is equal to 0.9.

Hence equation (3) is the general formula over a wide range of pressures. If the pressure is so low that the mean free path of the molecule is large against the diameter of the capillary, the first term of equation (3) can be neglected and γ becomes unity, so that the formula of pure molecular flow is obtained. If the pressure is so high that the mean free path is negligible against the diameter, the second term of equation (3) is negligible and we have the formula of pure viscous flow.

Knudsen[3] introduced empirically the following formula for γ and as the value at higher pressures gave 0.81 which is smaller than the value obtained by the present author.

$$\gamma = \frac{1+c_1 p}{1+c_2 p} \qquad (5)$$

where $$c_1 = 2.00\frac{\sqrt{\rho_1}}{\eta}r, \qquad c_2 = 2.47\frac{\sqrt{\rho_1}}{\eta}r.$$

The comparison between the values of γ calculated by (5) and those observed for hydrogen is graphically shown in Fig. 2.

As seen from Fig. 2, the observed values of γ can not be appropriately expressed by Knudsen's formula.

If only a fraction f of the impinging molecules leave the wall according to the cosine law and the remainder, 1—f, are regularly reflected, some factor must be introduced into the formula of the molecular flow. This factor was given as $(2-f)/f$ by Smoluchowski[4] and $f/(2-f)$ by Gaede.[5] As described in foregoing paper, this factor is unity at the pure molecular flow. However, if we assume that f is not unity at medium pressures, it will be able to interpret, by using Gaede's factor, that γ becomes smaller than unity. This assumption of f smaller than unity at medium pressures deserves further theoretical investigation.

The existence of a minimum point of the K–p curve seems to be peculiar and has been experimentally examined by many authors. However, as seen from the results of the present author, Knudsen, and Klose,[6] the existence is probably correct, notwithstanding that the theoretical interpretation has not yet been done.

There is a close connection between the decrease of the values of γ and the existence of a minimum point, and if the former can be interpreted, the latter point will be clear.

The Quantities of Flow of Gaseous Mixtures. The quantities of flow of the mixtures (K') of $H_2 \sim C_2H_2$ and $H_2 \sim C_3H_6$ were measured and the results are tabulated in Tables 3 and 4.

The shape of $K'-p$ curves of mixtures is similar to that of simple gases. As seen from the fourth columns of Tables 4 and 5, γ''s of mixtures, similarly as in the case of simple gases, become constant at higher pressures. Hence the quantity of flow of a mixture can be expressed by a formula analogous to (3), namely,

(3) M. Knudsen, *Ann. Physik*, (IV), **28** (1909), 75.
(4) M. v. Smoluchowski, *ibid.*, (IV), **33** (1910), 1559.
(5) W. Gaede, *ibid.*, (IV), **41** (1913), 289.
(6) W. Klose, *ibid.*, (V), **11** (1931), 73.

Table 3. The Quantities of Flow of $H_2 \sim C_2H_2$. (Fig. 3.)

Mixture I.
(H_2: 75.6%, C_2H_2: 24.31%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
2.780	0.0768	0.0445	0.72	
1.914	0.0665	0.0443	0.71	0.72
1.343	0.0601	0.0445	0.72	
0.725	0.0530	0.0446	0.72	
0.4756	0.0535	0.0480	0.77	
0.2730	0.0558	0.0526	0.85	
0.1458	0.0576	0.0559	0.90	
0.0581	0.0620	0.0613	0.99	
0.0503	0.0621	0.0615	0.99	
0.0221	0.0621	0.0619	1.00	

Mixture II.
(H_2: 51.18%, C_2H_2: 48.82%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.161	0.0730	0.0356	0.73	
2.064	0.0601	0.0357	0.73	0.73
1.422	0.0525	0.0357	0.73	
0.858	0.0458	0.0357	0.73	
0.518	0.0430	0.0369	0.75	
0.3281	0.0435	0.0396	0.81	
0.2002	0.0459	0.0435	0.89	
0.1471	0.0470	0.0453	0.92	
0.0659	0.0485	0.0477	0.97	
0.0374	0.0490	0.0485	0.99	

Mixture III.
(H_2: 25.97%, C_2H_2: 74.03%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
2.886	0.0624	0.0260	0.73	
1.944	0.0503	0.0258	0.73	0.73
0.925	0.0374	0.0257	0.73	
0.694	0.0345	0.0258	0.73	
0.4154	0.0322	0.0270	0.76	
0.2260	0.0317	0.0284	0.80	
0.1374	0.0320	0.0303	0.85	
0.0276	0.0341	0.0337	0.95	
0.0187	0.0352	0.0350	0.99	
0.0113	0.0354	0.0353	0.99	

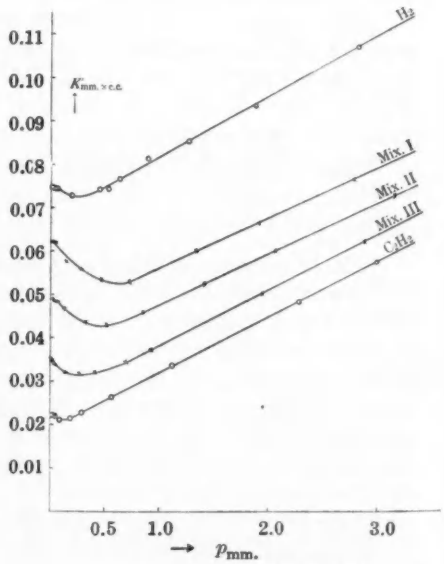


Fig. 3. $H_2 \sim C_2H_2$ (20°C.)

Table 4. The Quantities of Flow of $H_2 \sim C_3H_6$. (Fig. 4.)

Mixture I.

(H_2: 50.82%, C_3H_6: 49.18%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.000	0.0699	0.0302	0.66	
2.034	0.0570	0.0300	0.66	0.66
0.995	0.0431	0.0299	0.65	
0.591	0.0381	0.0303	0.66	
0.3013	0.0385	0.0345	0.75	
0.2093	0.0402	0.0374	0.82	
0.0980	0.0450	0.0437	0.95	
0.0619	0.0455	0.0447	0.98	
0.0390	0.0459	0.0454	0.99	
0.0128	0.0458	0.0456	1.00	

Mixture II.

(H_2: 75.18%, C_3H_6: 24.82%)

$p_{mm.}$	K'	$K'-a'p$	γ'	
3.008	0.0780	0.0401	0.66	
1.982	0.0648	0.0398	0.65	0.66
0.942	0.0510	0.0401	0.66	
0.710	0.0496	0.0406	0.67	
0.450	0.0518	0.0461	0.76	
0.2621	0.0550	0.0517	0.85	
0.1899	0.0588	0.0564	0.92	
0.0848	0.0603	0.0592	0.97	
0.0403	0.0609	0.0604	0.99	
0.0117	0.0610	0.0609	1.00	

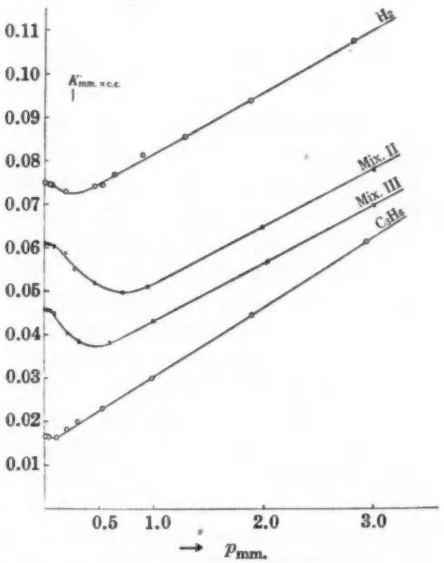


Fig. 4. $H_2 \sim C_3H_6$ (20°C.)

$$K' = a'p + \gamma' b', \qquad (6)$$

where $$a' = \frac{\pi}{8}\frac{1}{\eta'}\frac{r^4}{l}, \qquad b' = \frac{4}{3}\sqrt{2\pi}\frac{r^3}{l}\left(\frac{n_1}{\sqrt{\rho_1}} + \frac{n_2}{\sqrt{\rho_2}}\right),$$

n_1 and n_2 are mol fractions of components and the prime means the values of a mixture.

The comparison between the observed and calculated values of a' is given in Table 5.

Table 5.

		$\eta'_{20°} \times 10^7$	a' obs.	a' calc.	γ' at higher press.
$H_2 \sim C_2H_2$	Mixture I	1107	0.0116	0.0117	0.72
	Mixture II	1088	0.0118	0.0119	0.73 } 0.73
	Mixture III	1055	0.0126	0.0123	0.73
$H_2 \sim C_3H_6$	Mixture I	1082	0.0126	0.0120	0.66
	Mixture II	1011	0.0133	0.0128	0.66 } 0.66

The calculated values of a' are obtained by using the viscosities which are computed, in the case of $H_2 \sim C_2H_2$, by interpolation from the observed values at 20°C. and, in the case of $H_2 \sim C_3H_6$, by the viscosity formula for the mixture, the viscosities at 20° being not observed.

The values of γ' at higher pressures of the mixtures are summarized in the last column of Table 5. These are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases.

As seen from the K'–p curves in Fig. 3 and 4, the occurrence of minimum point of mixtures is very much remarkable. It was already shown in a preceding paper that when a mixture flows through the capillary, the separation takes place at low pressures, for example at the pressures lower than about 1 mm. for the mixture $H_2 \sim C_2H_2$. Owing to this separation the flow of hydrogen is comparatively larger at pressures lower than 1 mm., consequently the minimum point occurs at the pressure higher than in the case of simple gases.

The Quantities of Flow of Mixtures of Organic Vapours. The quantities of flow of the following mixtures of organic vapours were measured at the pressures lower than about 3 mm.

$$C_6H_6 \sim CCl_4, \quad CCl_4 \sim CHCl_3, \quad (C_2H_5)_2O \sim CHCl_3.$$

In order to increase the accuracy of measurement and to be able to compute the viscosities from K–p curves, the essential parts of the apparatus were kept in the thermostat and the McLeod gauge of short type was read by using a cathetometer. The experimental procedure is the same as described in the preceding paper.

The results of observation are shown graphically in Fig. 5–7. The flowing quantities of these mixtures can be expressed, similarly as the mixtures described above, by equation (6).

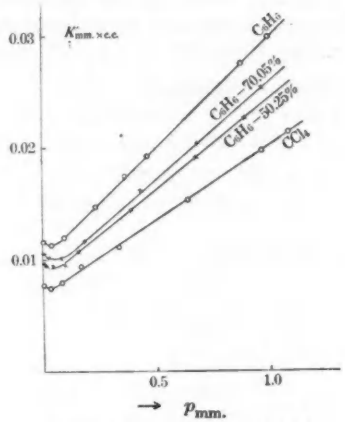


Fig. 5. $C_6H_6 \sim CCl_4$ (20°C.)

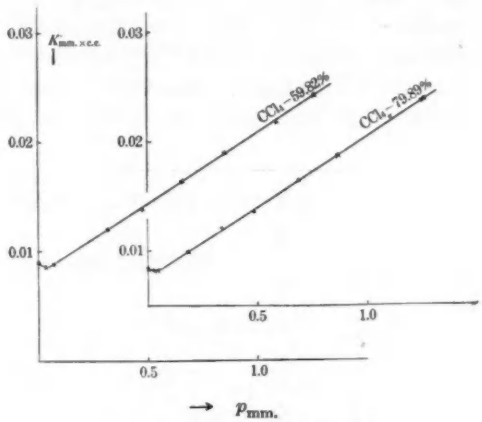


Fig. 6. $CCl_4 \sim CHCl_3$ (20°C.)

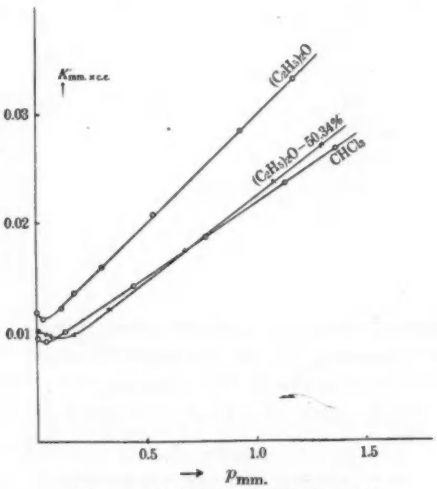
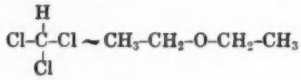
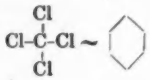
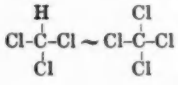


Fig. 7. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The values of γ' at higher pressures are 0.69 for $CHCl_3 \sim (C_2H_5)_2O$, 0.80 for $CCl_4 \sim C_6H_6$, and 0.89 for $CHCl_3 \sim CCl_4$. Those together with other two are summarized in Table 6. γ' are about 0.9 for simple gases but smaller for mixtures. It can be noticed that the value of γ' depends upon the configurations of two components. Namely as the configurations of $CHCl_3$ and CCl_4 are alike, the mixture of these vapours has the value

of γ' nearly equal to that of a simple gas. But the values of the mixtures of $H_2 \sim C_3H_6$ and $CHCl_3 \sim (C_2H_5)_2O$, whose components are considered to have not similar configurations, are far smaller than 0.9.

Table 6. The Values of γ' at Higher Pressures.

	γ' at higher press.
$H_2 \sim CH_3\text{-}CH{=}CH_2$	0.66
	0.69
$H_2 \sim CH{\equiv}CH$	0.73
	0.80
	0.89
H_2	0.91
C_2H_2	0.88
C_3H_6	0.90
C_6H_6	0.87
$CHCl_3$	0.90
CCl_4	0.88
$(C_2H_5)_2O$	0.86

The Viscosities of Benzene, Carbon tetrachloride, Chloroform, Ethyl ether, and Their Mixtures. From the quantities of flow the viscosities of the vapours can be calculated by equation (4). The values at 20°C. for C_6H_6, CCl_4, $CHCl_3$, and $(C_2H_5)_2O$ are given in Table 7.

Table 7.

Vapour	$\eta \times 10^7$ at 20°C.	
	obs.	calc.
C_6H_6	662	705
CCl_4	983	939
$CHCl_3$	976	971
$(C_2H_5)_2O$	666	695

The values given in the third column of Table 7 are calculated using Sutherland's constants obtained by T. Titani.[7] The agreement of the calculated and observed values is not good. This is perhaps due to the fact that Sutherland's constants were obtained from the observations above the boiling point and this constant is not satisfactorily accurate for low temperature.

The viscosities of mixtures of $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, and $(C_2H_5)_2O \sim CHCl_3$ are given in Tables 8–10 and Fig. 6–8.

Table 8. Viscosities of $C_6H_6 \sim CCl_4$ at 20°C. (Fig. 8.)

$$\eta' = \frac{662\times10^{-7}}{1+\frac{n_2}{n_1}1.0} + \frac{983\times10^{-7}}{1+\frac{n_1}{n_2}1.0}$$

C_6H_6 %	CCl_4 %	$\eta'\times10^7$ obs.	$\eta'\times10^7$ calc.
100.00	0.00	662	662
75.05	24.95	746	740
50.25	49.75	816	822
0.00	100.00	983	983

$\alpha_1\alpha_2\beta = 1.39$, $\alpha_1\alpha_2/\beta = 0.63$

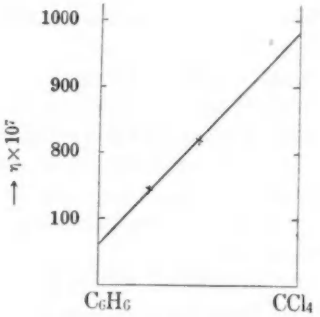


Fig. 8. $C_6H_6 \sim CCl_4$ (20°C.)

Table 9. Viscosities of $CCl_4 \sim CHCl_3$ at 20°C. (Fig. 9.)

$$\eta' = \frac{983\times10^{-7}}{1+\frac{n_2}{n_1}0.82} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.96}$$

CCl_4 %	$CHCl_3$ %	$\eta'\times10^7$ obs.	$\eta'\times10^7$ calc.
100.00	0.00	983	983
79.89	20.11	1020	1017
59.82	50.18	1038	1038
0.00	100.00	976	976

$\alpha_1\alpha_2\beta = 0.99$, $\alpha_1\alpha_2/\beta = 0.985$

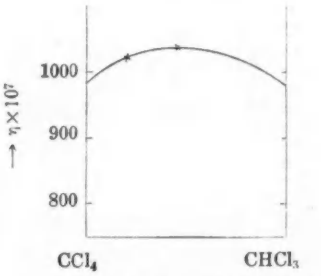


Fig. 9. $CCl_4 \sim CHCl_3$ (20°C.)

(7) T. Titani, this Bulletin, **8** (1933), 255.

Table 10. Viscosities of $(C_2H_5)_2O \sim CHCl_3$ at 20°C. (Fig. 10.)

$$\eta_l' = \frac{666\times10^{-7}}{1+\frac{n_2}{n_1}0.877} + \frac{976\times10^{-7}}{1+\frac{n_1}{n_2}0.982}$$

$(C_2H_5)_2O$%	$CHCl_3$ %	$\eta_l'\times10^7$	
		obs.	calc.
100.00	0.00	666	666
50.34	49.66	848	847
0.00	100.00	976	976
$\alpha_1\alpha_2\beta = 1.425, \quad \alpha_1\alpha_2/\beta = 0.66$			

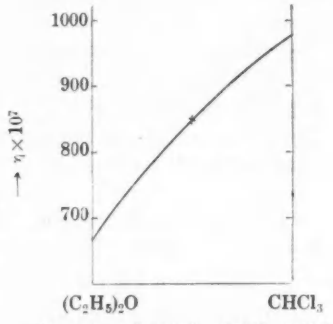


Fig. 10. $(C_2H_5)_2O \sim CHCl_3$ (20°C.)

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight. The occurrence of the maximum point in the case of $CCl_4 \sim CHCl_3$ is very well explained by the conditions theoretically discussed in the first paper of this series.

The values of Sutherland's constants between different molecules obtained from the viscosity data of mixtures are given in Table 11.

Table 11. Sutherland's Constants of Mixtures.

Mixture		C_1	C_2	C_{12}
1	2			
C_6H_6	CCl_4	448	365	720
CCl_4	$CHCl_3$	365	373	301
$CHCl_3$	$(C_2H_5)_2O$	373	404	352

Summary.

(1) The quantities of seven following simple gases and six gaseous mixtures flowing through the capillary have been measured at the pressures between 4 and 0.01 mm.

H_2, C_2H_2, C_3H_6, $H_2 \sim C_2H_2$, $H_2 \sim C_3H_6$;
C_6H_6, CCl_4, $CHCl_3$, $(C_2H_5)_2O$, $C_6H_6 \sim CCl_4$, $CCl_4 \sim CHCl_3$, $(C_2H_5)_2O \sim CHCl_3$.

(2) The quantities of flow, K, is a function of the mean pressure, p, and the K–p curve passes through a minimum point. The occurrence of a minimum point of mixtures is more remarkable than in the case of simple gases.

(3) The quantities of flow of simple gases are satisfactorily expressed by

$$K = \alpha p + \gamma b ,$$

where γ is a coefficient which becomes a constant at higher pressures ($= 0.9$) or at very low pressures ($= 1.0$), and varies from 0.9 to 1.0 at the intermediate conditions.

(4) The quantities of flow of mixtures are also expressed by a formula analogous to that of simple gases. The values of γ' at higher pressures of the mixtures are constant for varying compositions of the same combination of components, but different from those for different combinations and simple gases. These values are also considered to depend on the chemical configurations of two components.

(5) The viscosities of the following mixtures have been calculated from the quantities of flow.

$$C_6H_6 \sim CCl_4 , \qquad CCl_4 \sim CHCl_3 , \qquad (C_2H_5)_2O \sim CHCl_3 .$$

The mixture $CCl_4 \sim CHCl_3$ shows a maximum at about 50% of $CHCl_3$ and the viscosity curves of the other two are nearly straight.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

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On the Flow of Gases through a Porous Wall.

By Hiroshi ADZUMI.

(Received May 31st, 1937.)

The rate of flow of gases through a porous plate was studied by Sameshima[1] and the following formula was introduced empirically by him.

$$t = k\eta^n M^{\frac{1-n}{2}},$$

where t is the time of flow of a definite volume of the gas, η the viscosity, M the molecular weight of the gas, k and n are constants independent of the kind of the gas but dependent on the nature of the porous plate and the pressure of the gas.

It was reported by the present author[2] that, when a gas flows through a capillary, the quantity flowing in unit time is expressed by the following formula:

$$Q = K(p_1 - p_2)$$

$$\text{or} \qquad K = A\frac{r^4}{l}p + \gamma B\frac{r^3}{l} \quad (\text{in mm.} \times \text{c.c.}), \tag{1}$$

where $$A = 5.236 \times 10^2 \frac{1}{\eta}, \qquad B = 3.05 \times 10^4 \sqrt{\frac{T}{M}},$$

K is the quantity of flow for unit pressure difference, measured by the product of the pressure and the volume, l and r the length and the radius of the capillary, p_1 and p_2 the pressures (measured in mm.) at the ends of the capillary, p the mean of these, T the temperature and γ a coefficient depending on pressure. This formula holds generally over a wide range of pressure, namely for various values of the ratios of the mean free path of the gas and the diameter of the capillary.

A porous plate may be considered to be composed of numerous pores of various diameters. If the diameters of all pores are large against the mean free path, the part of the molecular flow becomes negligible, and if the diameters are small against the mean free path, pure molecular flow will take place. However, in the case of an actual porous plate, the

(1) J. Sameshima, this Bulletin, **1** (1926), 5.
(2) This Bulletin, **12** (1937), 292.

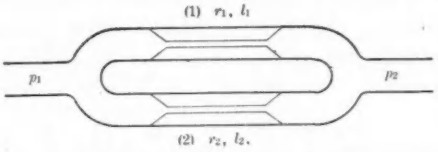
diameters of some pores may be large while those of others small against the mean free path.

Therefore, by using equation (1) we will be able to derive the formula of flow through a porous plate of any kind.

Flowing Formula of a Gas through a Porous Plate. We assume, before everything, that all pores of a porous plate are parallel and each pore may not have an uniform diameter but be composed of short pores of various diameters.

In order to know the flowing formula of a gas through a porous plate, we will treat, in the first place, the simple cases of the flow through many capillaries, whose radii and state of connection are known.

(i) **Flowing formula of a gas through numerous capillaries, which are connected in parallel.** When two capillaries, whose radii and lengths



are r_1, r_2 and l_1, l_2, are connected in parallel, the quantity flowing through capillary (1) in unit time and under unit pressure difference is given by

$$K_1 = A\frac{r_1^4}{l_1}p+\gamma B\frac{r_1^3}{l_1},$$

and the quantity through capillary (2) by

$$K_2 = A\frac{r_2^4}{l_2}p+\gamma B\frac{r_2^3}{l_2},$$

then the total quantity, K', becomes

$$K' = K_1+K_2 = A\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}\right)p+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}\right).$$

The validity of this equation was examined numerically by measuring the quantities of hydrogen through the following capillaries:

Capillary (1): $r_1 = 0.0121$ cm., $l_1 \fallingdotseq 8.7$ cm.,

,, (2): $r_2 = 0.0073$ cm., $l_2 \fallingdotseq 8.8$ cm.

The values of K_1, K_2, and K' are given in Table 1. In this table, for the convenience of comparison, the values of three kinds of K are obtained respectively by the interpolation for the same pressures.

Table 1.

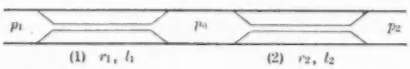
$p_{mm.}$	K_1	K_2	K_1+K_2	$K'_{obs.}$
3.0	0.1103	0.0181	0.1286	0.1285
2.0	0.0960	0.0170	0.1130	0.1132
1.0	0.0822	0.0160	0.0982	0.0980
0.8	0.0795	0.0154	0.0949	0.0950
0.6	0.0766	0.0150	0.0916	0.0917
0.4	0.0742	0.0147	0.0889	0.0889
0.2	0.0730	0.0144	0.0874	0.0865
0.1	0.0737	0.0155	0.0892	0.0890
0.05	0.0745	0.0164	0.0909	0.0905

As seen from Table 1, the observed values of K' agree very well with those calculated by the equation. Hence, when numerous capillaries, whose radii and lengths are r_1, r_2, r_3, ... r_n, and l_1, l_2, l_3, ... l_n, are connected in parallel, the quantity of flow is expressed by

$$K' = A\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}+\frac{r_3^4}{l_3}+\cdots\right)p+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}+\frac{r_3^3}{l_3}+\cdots\right)$$

$$= Ap\sum^{n}\frac{r_i^4}{l_i}+\gamma B\sum^{n}\frac{r_i^3}{l_i}\,. \qquad (2)$$

(ii) **Flowing formula through numerous capillaries, which are connected in series.** When two capillaries are connected in series, we



denote the pressure between the capillaries as p_0. The quantity flowing through capillary (1) in unit time is given by

$$Q_1 = A\frac{r_1^4}{l_1}\,\frac{p_1+p_0}{2}(p_1-p_0)+\gamma B\frac{r_1^3}{l_1}(p_1-p_0)\,,$$

and that through capillary (2) by

$$Q_2 = A\frac{r_2^4}{l_2}\,\frac{p_0+p_2}{2}(p_0-p_2)+\gamma B\frac{r_2^3}{l_2}(p_0-p_2)\,.$$

As these two quantities are equal, then

$$Q'' = K''(p_1-p_2) = Q_1 = Q_2\,,$$

where K'' is the quantity flowing in unit time and under unit pressure difference through two capillaries connected in series,

From these three formulæ

$$\frac{1}{K''} = \frac{1}{K_1 + A\frac{r_1^4}{l_1}\frac{p_0-p_2}{2}} + \frac{1}{K_2 - A\frac{r_2^4}{l_2}\frac{p_1-p_0}{2}},$$

where K_1 and K_2 are the quantities flowing through capillaries (1) and (2) respectively, when each of them is alone.

Thus when two capillaries are connected in series, $1/K''$ is not equal to $(1/K_1 + 1/K_2)$.

By eliminating p_0, $1/K''$ is also written in the form

$$\frac{1}{K''} = \frac{1}{K_1} + \frac{1}{K_2} + \Delta_1,$$

where $$\Delta_1 = \frac{(c_2d_1 - c_1d_2)/c_1}{K_1K_2} \cdot \frac{1}{1 + \dfrac{2K_1(c_1+c_2)/c_1}{(c_1+c_2)-(K_1+K_2)+\sqrt{\{(K_1-K_2)+(c_1+c_2)\}^2+4K_1K_2}}},$$

$$c_1 = \frac{1}{2}A\frac{r_1^4}{l_1}, \quad c_2 = \frac{1}{2}A\frac{r_2^4}{l_2}, \quad d_1 = \gamma B\frac{r_1^3}{l_1}, \quad d_2 = \gamma B\frac{r_2^3}{l_2}.$$

The value of Δ_1 is estimated, by inserting numerical values, to be so small that it affects the value of K'' only less than 1%. Then, by neglecting Δ_1

$$K'' = \frac{1}{\frac{1}{K_1}+\frac{1}{K_2}} = Ap\frac{1}{\frac{l_1}{r_1^4}+\frac{l_2}{r_2^4}} + \gamma B\frac{1}{\frac{l_1}{r_1^3}+\frac{l_2}{r_2^3}} + \Delta_2,$$

where $$\Delta_2 = \frac{Ap\cdot\gamma B\left(\frac{r_1^3}{l_1}\frac{r_2^3}{l_2}\right)^2(r_1-r_2)^2}{\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}\right)\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}\right)\left\{Ap\left(\frac{r_1^4}{l_1}+\frac{r_2^4}{l_2}\right)+\gamma B\left(\frac{r_1^3}{l_1}+\frac{r_2^3}{l_2}\right)\right\}}.$$

Δ_2 is also found under ordinary experimental conditions to have a value smaller than 1% of the other terms. Then we have

$$K'' = Ap\frac{1}{\frac{l_1}{r_1^4}+\frac{l_2}{r_2^4}} + \gamma B\frac{1}{\frac{l_1}{r_1^3}+\frac{l_2}{r_2^3}}.$$

Table 2.

$p_{mm.}$	K''	
	obs.	calc.
3.0	0.0159	0.0165
2.0	0.0144	0.0148
1.0	0.0130	0.0133
0.5	0.0199	0.0123
0.1	0.0128	0.0128
0.05	0.0129	0.0129

This equation was examined numerically by using the two capillaries described above. (Table 2.)

It will be seen from the table, that the results are satisfactorily expressed by the above equation justifies the neglections made in obtaining it.

When numerous capillaries are connected in series, the quantity of flow is expressed by

$$K'' = A\frac{1}{\sum^{m}\frac{l_i}{r_i^4}}p+\gamma B\frac{1}{\sum^{m}\frac{l_i}{r_i^3}} . \qquad (3)$$

As it was assumed, if all pores of a porous plate are parallel and each pore is composed of series of short pores having various diameters, the quantity of a gas flowing through a porous plate can be expressed by the combination of equations (2) and (3) as follows:

$$K = Ap\sum^{n}\frac{1}{\sum^{m}\frac{l_i}{r_i^4}}+\gamma B\sum^{n}\frac{1}{\sum^{m}\frac{l_i}{r_i^3}} ,$$

or $$K = ApE+\gamma BF$$

$$= 5.236\times 10^2\frac{1}{\eta}Ep+2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in mm.} \times \text{c.c.)}, \quad (4_1)$$

where $E = \sum\frac{1}{\sum\frac{l_i}{r_i^4}}$, $F = \sum\frac{1}{\sum\frac{l_i}{r_i^3}}$, and γ is taken as 0.9. E and F are functions of the radii and lengths of pores. The actual construction of pores is so complicated that the functional forms of these coefficients can not be obtained directly. If pressures are measured in atmospheric unit, the above equation becomes

$$K = 3.979\times 10^5\frac{1}{\eta}Ep+2.743\times 10^4\sqrt{\frac{T}{M}}F \text{ (in atm.} \times \text{c.c.)}. \quad (4_2)$$

Equation (4) was examined numerically by measuring the quantities of flow through a few kinds of porous plates. As an example, the results of comparison between the values observed by Sameshima[1] and those

of calculated by (4) are given in Table 3. Sameshima measured the time of flow of a definite volume (ca. 70 c.c.) of seven gases at the following pressures: $p_1 = 1.0, 1.5, 2.0, 2.5$ atm.; $p_2 = 0$; so that $p = 0.5, 0.75, 1.0, 1.25$ atm. By the method of least square, the values of two constants E and F were obtained as follows: $E = 1.83 \times 10^{-11}$, $F = 3.45 \times 10^{-7}$. Hence the flowing formula of a gas at 25°C. through the porous plate (an unglazed earthen-ware) used by Sameshima becomes

$$K = 7.282 \times 10^{-6} \frac{1}{\eta} p + 1.636 \times 10^{-1} \frac{1}{\sqrt{M}} \quad \text{(in atm.} \times \text{c.c.)}.$$

This formula was used for the calculation of the values of K given in Table 3.

Table 3. The Quantities of Flow of Gases through the Porous Plate observed by Sameshima.

$P_{atm.}$	0.5		0.75	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.0728	0.0735	0.0892	0.0898
NH_3	0.0742	0.0747	0.0919	0.0922
C_2H_2	0.0668	0.0672	0.0844	0.0847
C_2H_4	0.0648	0.0669	0.0825	0.0849
Air	0.0495	0.0504	0.0600	0.0603
O_2	0.0460	0.0465	0 0552	0.0552
CO_2	0.0480	0.0482	0.0602	0.0600
$P_{atm.}$	1.0		1.25	
	K		K	
	obs.	calc.	obs.	calc.
CH_4	0.1054	0.1061	0.1220	0.1224
NH_3	0.1098	0.1096	0.1276	0.1282
C_2H_2	0.1021	0.1023	0.1200	0.1198
C_2H_4	0.1000	0.1029	0.1167	0.1209
Air	0.0698	0.0702	0.0798	0.0802
O_2	0.0642	0.0640	0.0732	0.0727
CO_2	0.0724	0.0717	0.0844	0.0834

As seen from Table 3, the quantity of a gas flowing through the porous plate is expressed satisfactorily by equation (4).

The present author with M. Tachimori measured also the quantities of flow through a few kinds of porous plates and found that the quantities

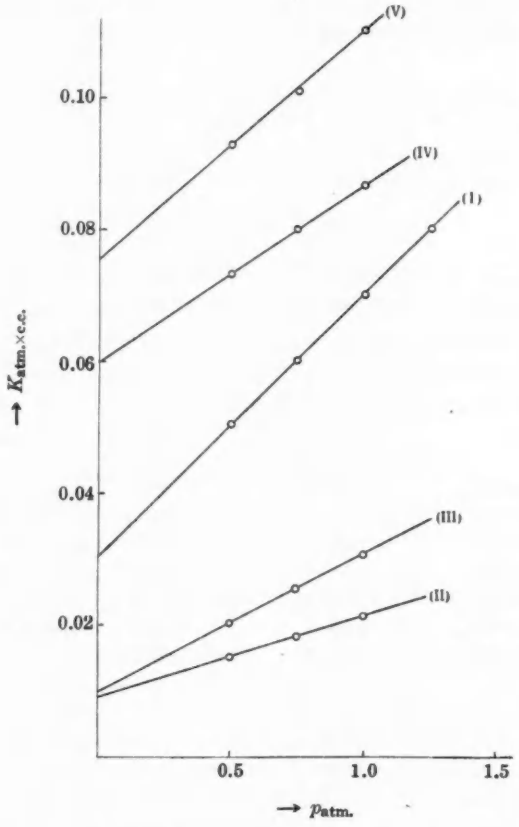


Fig. 1. Quantities of Air Flowing through Porous Plates.

are also expressed by equation (4). The results are represented graphically in Fig. 1.

The values of E and F for the several porous plates and gases used for experiments are tabulated in Table 4.

Table 4.

Porous plate	Gas	Temp.	$E\times10^{11}$	$F\times10^{7}$
(I) Unglazed earthen-ware used by Sameshima	CH_4, etc.	25°C.	1.83	3.45
(II) Porous plate used in organic preparation (compact)	Air	20	0.45	1.64
(III) ,, (rough)	Air	20	0.83	1.72
(IV) Mantle of a Daniell cell (white)	Air	25	1.1	6.82
(V) ,, (red)	Air	25	1.5	8.58

Mean Radius and Number of Pores per unit Area of a Porous Matter. For many purpose it is sufficient to know the mean value of the pore radii of porous matters, for example unglazed earthen-wares, glass-filters, filterpapers, membranes of colloidon, etc. As already pointed out, the construction of pores of a porous matter is so complicated that we can not find any method to obtain the actual radius and number of pores. Therefore, in order to estimate the radius, we must take some simplifications about the construction of pores. The simplest assumption is that each pore has an uniform radius. Several methods of obtaining the radius, under this assumption, have been introduced. Bartell and Osterhof[3], and Uehara[4] obtained the radii of porous matters by measuring the pressure necessary to prevent ascension of a liquid in the capillaries and Anderson[5] by measuring the change of the vapour pressure in the capillaries. Kawakami[6] estimated them from the measurements of the quantity of effusion, the electric conductivity, and the maximum linear velocity of a liquid in a porous matter.

If all pores of the porous plate have the uniform radius, R, and are normal to the surface, E and F can be written in a very simple form as follows:

$$E = nR^4/d\,, \qquad F = nR^3/d\,,$$

where n is the number of pores and d the thickness of the porous plate. Hence, E and F are proportional to the area of the surface and inversely proportional to the thickness of the plate, so that the values for unit area

(3) F. E. Bartell and H. J. Osterhof, *J. Phys. Chem.*, **32** (1928), 1553.
(4) K. Uehara, *J. Chem. Soc. Japan*, **55** (1934), 75.
(5) J. S. Anderson, *Z. physik. Chem.*, **88** (1914), 191.
(6) M. Kawakami, *J. Chem. Soc. Japan*, **53** (1932), 1085; **54** (1933), 133.

and unit thickness, E_0, F_0, can be easily obtained by $E_0 = Ed/\text{area}$, $F_0 = Fd/\text{area}$.
Then we have

$$E_0 = NR^4 \quad \text{and} \quad F_0 = NR^3 ,$$

where N is the number of pores per unit area of the surface.
From these formulæ,

$$R = E_0/F_0 , \qquad N = F_0^4/E_0^3 . \tag{5}$$

The values of R and N for several porous plates calculated by equation (5) are given in Table 5.

Table 5. Mean Diameters of Pores and Number of Pores per Unit Area.

Porous plate	Thickness	Area	$E_0\times10^{11}$	$F_0\times10^7$	$R\times10^5$ cm.	N
(I)	0.15 cm.	0.28 cm.^{2}	0.97	1.83	5.3	1.2×10^6
(II)	0.27	2.22	0.054	0.195	2.77	2.4×10^5
(III)	0.41	2.22	0.154	0.318	4.84	2.8 ,,
(IV)	0.2	0.27	0.80	4.98	1.61	0.96×10^6
(V)	0.2	0.27	1.09	6.26	1.74	1.19 ,,

Summary.

(1) A formula for the flow of a gas through a porous plate has been derived and found that the observed quantity of flow is satisfactorily expressed by this formula.

(2) The method of estimating the values of the mean radius and the number of pores of a porous plate has been proposed.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his encouragement throughout this experiment.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

Chemical Reactions in the Silent Electric Discharge. XVI. Reactions between Hydrogen and Solid Inorganic Compounds.

By Susumu MIYAMOTO.

(Received April 16th, 1937.)

Studies on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out; there follows an account of the results obtained since the publication of the previous papers.[1]

(1) Potassium chromate. It was proved that chromic oxide is a principal reaction product. Potassium chromate employed = 5 g. Time of silent electric discharge = 12 hours. The quantity of chromic oxide produced = 0.1083 g.

The principal reaction in the discharge tube is expressed by

$$2K_2CrO_4 + 3H_2 = 4KOH + Cr_2O_3 + H_2O\,.$$

(2) Potassium bichromate. Potassium bichromate is reduced to chromic oxide also. Potassium bichromate employed = 5 g. Time of silent electric discharge = 12 hours. The quantity of chromic oxide produced = 0.0463 g.

The principal reaction in the discharge tube is expressed by

$$K_2Cr_2O_7 + 3H_2 = 2KOH + Cr_2O_3 + 2H_2O\,.$$

(3) Ammonium chromate. A gas absorption bottle, containing dilute sulphuric acid solution, was connected to the discharge tube, and the quantity of ammonia absorbed was determined in the normal manner. Ammonium chromate employed = 5 g. Time of silent electric discharge = 8 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed = 6.68 c.c. The quantity of chromic oxide produced = 0.0357 g.

The principal reaction in the reaction tube is expressed by

$$2(NH_4)_2CrO_4 + 3H_2 = 4NH_3 + Cr_2O_3 + 5H_2O\,.$$

(4) Ammonium bichromate. Ammonium bichromate employed = 5 g. Time of silent electric discharge = 12 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonia absorbed = 3.21 c.c. The quantity of chromic oxide produced = 0.0210 g.

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320, 1143; **56** (1935), 521; this Bulletin, **9** (1934), 139, 165, 175, 505; **10** (1935), 199.

The principal reaction is expressed by

$$(NH_4)_2Cr_2O_7 + 3H_2 = 2NH_3 + Cr_2O_3 + 4H_2O\,.$$

(5) Calcium chlorate. Calcium chlorate is reduced to chloride in the discharge tube. The quantity of chloride produced was determined in the normal manner. Calcium chlorate employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of calcium chloride produced = 37.40 c.c.

The reaction in the discharge tube is expressed by

$$Ca(ClO_3)_2 + 6H_2 = CaCl_2 + 6H_2O\,.$$

(6) Sodium chlorate. Sodium chlorate employed = 7 g. Time of silent electric discharge = 6 hours. Volume of the silver nitrate solution of 0.01000 normal, equivalent to the quantity of sodium chloride produced = 28.50 c.c.

The reaction in the discharge tube is expressed by

$$NaClO_3 + 3H_2 = NaCl + 3H_2O\,.$$

(7) Barium sulphite. It was proved that barium sulphide and hydrogen sulphide are the principal reaction products. The reactions in the discharge tube will be expressed by

$$BaSO_3 + 3H_2 = BaS + 3H_2O\,,$$
$$BaS + 2H_2O = Ba(OH)_2 + H_2S\,,$$
$$BaS + H_2 = Ba + H_2S\,.$$

(8) Thorium nitrate. Exp. 1. The formation of thorium hydroxide, ammonium salt and nitrite was proved.

Exp. 2. The quantity of ammonium salt produced was determined in the normal manner. Thorium nitrate, $Th(NO_3)_4 \cdot 12H_2O$, employed = 5 g. Time of silent electric discharge = 6 hours. Volume of the sulphuric acid solution of 0.1000 normal, equivalent to the quantity of ammonium salt produced = 8.12 c.c.

Exp. 3. The quantity of nitrite produced was determined. Thorium nitrate employed = 5 g. Time of silent electric discharge = 6 hours. Volume of the potassium permanganate solution of 0.0100 normal, equivalent to the quantity of nitrite produced = 7.78 c.c.

The reactions in the discharge tube will be expressed by

$$Th(NO_3)_4 + 16H_2 = Th(OH)_4 + 4NH_3 + 8H_2O\,,$$
$$Th(NO_3)_4 + 4NH_3 + 4H_2O = 4NH_4NO_3 + Th(OH)_4\,,$$
$$NH_4NO_3 + H_2 = NH_4NO_2 + H_2O\,.$$

(9) Ammonium persulphate. It was proved that sulphate and hydrogen sulphide are the principal reaction products. The reactions in the reaction tube will be expressed by

$$(NH_4)_2S_2O_8 + 5H_2 = (NH_4)_2SO_4 + H_2S + 4H_2O,$$
$$(NH_4)_2S_2O_8 + H_2 = (NH_4)_2SO_4 + H_2SO_4.$$

(10) Potassium persulphate. The formation of sulphate and hydrogen sulphide was proved. The velocity of the reaction was very small. The reactions in the discharge tube will be expressed by

$$K_2S_2O_8 + 5H_2 = K_2SO_4 + H_2S + 4H_2O,$$
$$K_2S_2O_8 + H_2 = K_2SO_4 + H_2SO_4.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacts with the following inorganic solid substances.

Reacting substance	Reaction products
(1) Potassium chromate	Chromic oxide and potassium hydroxide
(2) Potassium bichromate	Chromic oxide and potassium hydroxide
(3) Ammonium chromate	Chromic oxide and ammonia gas
(4) Ammonium bichromate	Chromic oxide and ammonia gas
(5) Calcium chlorate	Calcium chloride
(6) Sodium chlorate	Sodium chloride
(7) Barium sulphite	Barium sulphide and hydrogen sulphide
(8) Thorium nitrate	Thorium hydroxide, nitrite and ammonium salt.
(9) Ammonium persulphate	Sulphate and hydrogen sulphide,
(10) Potassium persulphate	Sulphate and hydrogen sulphide.

The author acknowledges with thanks the receipt of a grant from the Imperial Academy of Japan.

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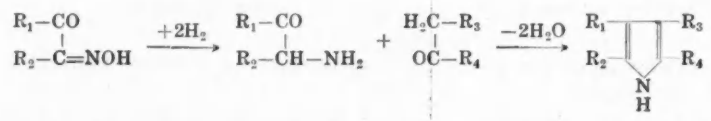
Ein neues Verfahren zur Synthese von Pyrrol-Derivaten.

Von Bun-ichi TOI und Shiro AKABORI.

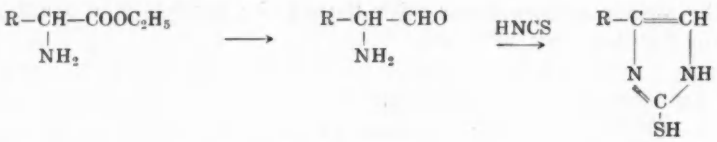
(Eingegangen am 28. Mai 1937.)

Für die Synthese der Pyrrol-derivate wendet man fast ausschliesslich die Knorrsche Methode[1] an, die auf der Kondensation von Aminoketonen mit Ketonen beruht. Bei der praktischen Ausführung der Synthese geht man aber zumeist von einem äquimolekularen Gemenge von Isonitrosoketonen und Ketonen aus. Wenn man das Gemenge in essigsaurer Lösung mittels Zinkstaub reduziert, so verläuft die Reaktion nach dem folgenden, allgemein gültigen Schema:



Es ist aber sehr wahrscheinlich, dass man an Stelle von Aminoketonen Aminoaldehyd anwenden kann, wenn diese Verbindungen auch im allgemeinen schwer zugänglich sind.

Einer der Verfasser (S. Akabori)[2] hat vor einigen Jahren ein allgemeines Verfahren für die Imidazolsynthese aus α-Aminosäuren eingeführt, indem er α-Aminosäureester mit Natriumamalgam zu α-Aminoaldehyd reduzierte und diesen mit Rhodanwasserstoffsäure zu Thiolimidazol kondensierte:

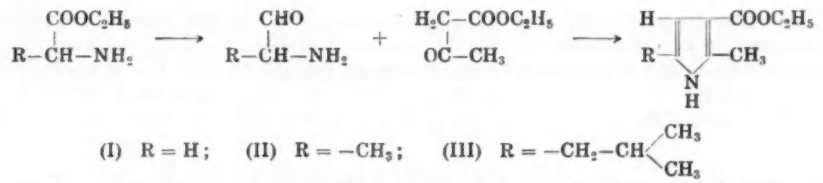


Wir konnten nun bei der Kondensation von Aminoaldehyden, die wir durch Reduktion von Aminosäureestern erhalten hatten, mit Acetessigester einige Pyrrol-derivate erhalten.

Die Reaktion geht im allgemeinen nach dem folgenden Schema vor sich:

(1) L. Knorr, *Ann.*, **236** (1886), 326.

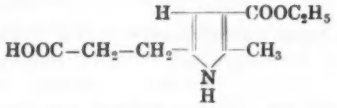
(2) S. Akabori, *Ber.*, **66** (1933), 152; S. Akabori und S. Numano, *Ber.*, **66** (1933), 159.



(I) R = H; (II) R = $-CH_3$; (III) R = $-CH_2-CH(CH_3)_2$

So gewinnt man aus Glykokoll 2-Methyl-3-carbäthoxy-pyrrol (I), aus Alanin 2,5-Dimethyl-3-carbäthxoy-pyrrol (II), aus Leucin 2-Methyl-3-carbäthoxy-5-isobutyl-pyrrol (III).

Interessanterweise erhält man aus Glutaminsäure 2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure (IV),



IV,

die ein Carbäthoxyderivat eines Isomers der Opsopyrrolcarbonsäure ist.

III und IV sind zwei bisher noch nicht in der Literatur beschriebene Pyrrol-derivate.

Beschreibung der Versuche.

2-Methyl-3-carbäthoxy-pyrrol (I). 14 g. Glykokollester-chlorhydrat wurden in 150 c.c. Alkohol und 100 c.c. Wasser gelöst, mittels Kältemischung auf $-10°$ abgekühlt und dann unter stetigem Rühren 400 g. 2.3%iges Natriumamalgam in kleinen Portionen eingeworfen. Während der Reduktion wurden, um die Lösung stets sauer zu halten, 80 c.c. 5 N Salzsäure zugetropft.

Die Reaktionsflüssigkeit wurde vom Quecksilber getrennt, filtriert, unter vermindertem Druck unterhalb 50° auf ca. 100 c.c. eingeengt und von ausgeschiedenem Kochsalz durch Filtrieren abgetrennt. Die so erhaltene Aminoaldehyd-lösung wurde mit 13 g. Acetessigester versetzt und 5 N Natriumhydroxyd zugefügt, bis die Lösung alkalisch reagierte.

Das Reaktionsprodukt wurde mit Äther ausgezogen und nach dem Trocknen mit wasserfreiem Natriumsulfat der Äther bis auf 15 c.c. abdestilliert. Beim Stehen der konzentrierten ätherischen Lösung im Eisschrank schieden sich Kristalle aus, die nach wiederholtem Umkrystallisieren aus verdünntem Alkohol bei 78–78.5° schmolzen. Ausbeute 1.5 g. Sie sind leicht löslich in Alkohol und Äther, schwerlöslich in kaltem Wasser. Die Analysenwerte stimmten mit den für 2-Methyl-3-carbäthoxy-pyrrol berechneten überein (Gefunden: C, 62.80, 62.76; H, 7.43, 7.20; N, 9.27. Ber. für $C_8H_{11}O_2N$: C, 62.71; H, 7.24; N, 9.15%). Nach E. Benary[3] schmilzt 2-Methyl-3-carbäthoxy-pyrrol bei 78–79°.

2,5-Dimethyl-3-carbäthoxy-pyrrol (II). 15.5 g. *dl*-Alaninäthylester-chlorhydrat wurden in gleicher Weise wie Glykokolläthylester-chlorhydrat mit 400 g. 2.3%igem

(3) *Ber.*, **44** (1911), 495.

Natriumamalgam reduziert und mit 13 g. Acetessigester versetzt, wobei 3 g. krystallinisches Kondensationsprodukt erhalten werden konnten. Nach mehrmaligem Umkrystallisieren aus 70%igem Alkohol schmolz es bei 117–117.5°. Der Schmelzpunkt steht mit dem in der Literatur gegebenen[4] im guter Übereinstimmung (Gefunden: C, 64.39, 64.23; H, 7.71, 7.45; N, 8.48. Ber. für $C_9H_{13}O_2N$: C, 64.63; H, 7.84; N, 8.38%).

2-Methyl-3-carbäthoxy-5-isobutyl-pyrrol (III). 20 g. *dl*-Leucinäthylester-chlorhydrat wurden in gleicher Weise wie Alaninäthylester-chlorhydrat mit 400 g. 2.3%igem Natriumamalgam reduziert und mit 13 g. Acetessigester versetzt, wobei sich 2 g. krystallinisches Kondensationsprodukt erhalten liessen.

Nach mehrmaligem Umkrystallisieren aus 70%igem Alkohol schmolz es bei 66.5–67.5° (Gefunden: C, 68.83, 69.07; H, 9.31, 9.04; N, 6.83. Ber. für $C_{12}H_{19}O_2N$: C, 68.85; H, 9.16; N, 6.70%).

2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure (IV). 15 g. Glutaminsäure wurden unter vermindertem Druck 3 Stunden bei 160–180° gehalten und so in Pyrrolidoncarbonsäure übergeführt. Dann gab man 200 c.c. absoluten Alkohol hinzu, sättigte bei Zimmertemperatur mit trocknem Chlorwasserstoff und kochte 4 Stunden auf dem Wasserbade. Nachdem man den Alkohol unter vermindertem Druck abdestilliert hat, wurde das zurückgebliebene sirupöse Glutaminsäurediäthylester-hydrochlorid wieder in absolutem Alkohol aufgelöst.

150 c.c. der alkoholischen Lösung, die 15 g. Glutaminsäure entsprechen, wurden mit 100 c.c. Wasser verdünnt und mittels Kältemischung unterhalb −10° abgekühlt; dann wurf man unter heftigem Rühren 400 g. 2.3%iges Natriumamalgam innerhalb ungefähr 1 Stunde in kleinen Portionen ein; gleichzeitig fügte man 5 N Salzsäure tropfenweise hinzu, um die Lösung sauer zu halten. Man fuhr mit dem Rühren noch ½ Stunde fort und filtrierte dann die vom Quecksilber abgetrennte Lösung.

Das Filtrat wurde unter vermindertem Druck unterhalb 50° auf ca. 100 c.c. eingeengt und von dem ausgeschiedenen Kochsalz durch Filtrieren getrennt. Die so erhaltene Aminoaldehyd-lösung wurde mit 13 g. Acetessigester versetzt, 5 N Natriumhydroxyd hinzugefügt, bis die Lösung alkalisch reagierte, und dann mittels Salzsäure auf etwa $pH = 3$ eingestellt. Das Reaktionsprodukt wurde mit Äther ausgezogen und nach dem Trocknen mit wasserfreiem Natriumsulfat der Äther bis auf 15 c.c. abdestilliert. Beim Stehen der konzentrierten ätherischen Lösung im Eisschrank schieden sich die Kristalle aus, die nach wiederholtem Umkrystallisieren aus 70%igem Alkohol bei 176–177° schmolzen; Ausbeute 2.5 g. Sie sind leicht löslich in Alkohol und Äther, schwer löslich in Wasser. Die Analysenwerte stimmten mit den für 2-Methyl-3-carbäthoxy-pyrrol-5-propionsäure berechneten überein (Gefunden: C, 58.64, 58.60; H, 6.12, 6.41; N, 5.97. Ber. für $C_{11}H_{15}O_4N$: C, 58.63; H, 6.72; N, 6.22%).

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(4) A. Hantzsch, *Ber.*, **23** (1890), 1474; H. Fischer und Heyse, *Ann.*, **439** (1924), 254.

Über die chemische Natur des Papains.

Von Shigeo MAEDA.

(Eingegangen am 28. Mai 1937.)

Willstätter und Grassmann haben die ersten sorgfältigen Untersuchungen über das Papain angestellt. Sie fanden[1], dass die Aktivierung des Papains mit HCN mit der Beziehung zwischen Enterokinase und Tryptase[2] grosse Ähnlichkeit hat. Der wichtigste Befund der genannten Autoren ist der, dass die Spezifität des nativen Papains von der des aktivierten Enzyms deutlich verschieden ist. Z.B. spaltet das native Papain Gelatine und nicht Pepton; Papaincyanhydrin dagegen spaltet die beiden Substrate.

Vor einigen Jahren hat W. Grassmann angegeben, dass in Papainpräparaten eine schwefelhaltige Verbindung vorkommt, die unter dem Einfluss von Cyanwasserstoff in eine SH-Verbindung von phytokinaseartiger Wirkung übergeht[3].

Diese Vorstellung wurde durch E. Maschmann[4] eingehend experimentell bestätigt. Die Weiterentwicklung dieser Anschauung, besonders auf Grund von Befunden über teilweise reversible Inaktivierung mit Oxydationsmitteln, führte ihn zur Postulierung der Thiolnatur für das Papain[5]. Th. Bersin hat angenommen, dass die die Aktivität hervorrufenden SS- und SH-Gruppen wie beim Insulin in die Peptidkette des Papainmoleküls eingebaut sind[6].

$$\underset{\text{(aktiv)}}{\text{Papain (Pa-SH)}} \underset{\text{HCN, } H_2S\text{, GSH}}{\overset{H_2O_2\text{, Jod, } SeO_3}{\rightleftharpoons}} \underset{\text{(inaktiv)}}{\text{Oxydiertes Papain (Pa-S-S-Pa)}}$$

Im Rahmen dieser Forschung ist von E. Maschmann[7] in einer gründlichen Untersuchung die Frage erörtert worden, welche Rolle ein "Begleitstoff-X" für die Proteolyse spielt, der Papainpräparaten durch wässrigen Alkohol entzogen werden kann. Er kommt zu dem Ergebnis,

(1) R. Willstätter und W. Grassmann, *Z. physiol. Chem.*, **138** (1924), 184.
(2) E. Waldschmidt-Leitz, *Z. physiol. Chem.*, **132** (1923-1924), 181.
(3) W. Grassman, *Z. angew. Chem.*, **44** (1931) 105.
(4) *Z. physiol. Chem.*, **219** (1933), 99; **228** (1934), 141; *Biochem. Z.*, **277** (1935), 97.
(5) *Z. physiol. Chem.*, **220** (1933), 209; **222** (1933), 177; *Ergeb. Enzymforsch.*, **4** (1935), 68.
(6) *Z. physiol. Chem.*, **233** (1935), 59.
(7) *Z. physiol. Chem.*, **228** (1934). 141.

dass der "Begleitstoff-X" mit S-S-Glutathion nicht identisch ist, aber ein noch unbekanntes disulfidhaltiges Polypeptid sein kann[8]. W. Grassmann[9] hat den schwefelhaltigen Begleitstoff des Papains nach vorausgegangener Reduktion mit Schwefelwasserstoff auf Grund seiner Löslichkeit in 70%igem Alkohol vom Enzym abgetrennt und gefunden, dass die so gewonnenen Akitivatorfraktionen zum wesentlichen Teil aus einem oder mehreren Cystein-Glutaminsäurepeptiden bestehen. Auf Grund dieser Tatsache könnte man zu dem Schluss geführt werden, dass die Postulierung der Thiolnatur für das Papain nach Bersin zum mindesten unwahrscheinlich ist, und dass vielmehr ein spezifischerer, SH-Gruppen tragender Begleitstoff, dessen Existenz für die Aktivierung des Enzyms notwendig ist, im Papainpräparat vorkommt[10].

M. Bergmann und Mitarbeiter[11] wollen durch teilweise Inaktivierung des Papains mit verschiedenen Reagenzien und darauffolgende Reaktivierung das Vorkommen von zwei Peptidasen und einer Proteinase im gewöhnlichen Papainpräparat festgestellt haben, und zwar soll nur eine von beiden Peptidasen durch Phenylhydrazin oder Hydroxylamin inaktiviert werden und dieselbe daher ein Carbonylgruppen enthaltendes Enzym sein. Nach den genannten Autoren soll aber im Proteinase-anteil kein Carbonylgruppen enthaltendes Enzym sein, weil es durch Phenylhydrazin nicht inaktiviert wird.

Der Verfasser hat auch die vorliegende Arbeit zu dem Zwecke unternommen, die stoffliche Natur des Papains auf chemische und enzymatische Weise zu untersuchen.

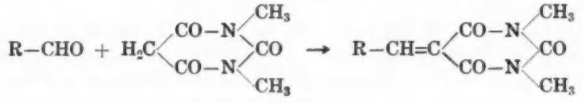
Wurde Handelspapain in Wasser gelöst und durch eine Kolloidiumhülse dialysiert, so verminderte sich dabei die Aktivität des Papains stark, konnte aber durch Zugabe von Cyanwasserstoff in hohem Masse reaktiviert werden. Die Aussenflüssigkeit der Dialyse wies keine enzymatische Wirkung auf. Aus der Innenlösung wurde durch Fällung mit Methanol ein Enzym-präparat gewonnen, das 15.02% N enthielt. Es war eine gelatineartige amorphe Masse, die sich durch relativ hohen Gehalt an Tryptophan (3.43%) auszeichnete und deren relative Aktivität vor und nach der Aktivierung mit Cyanwasserstoff 0.44 und 1.66 betrug.

Der Verfasser hat die Wirkungen verschiedener Reagenzien, nämlich Hydrazin, Phenylhydrazin, Hydroxylamin, Natriumbisulfit und Dimethylbarbitursäure, auf das Papain geprüft. Die Hemmungswirkung der

(8) *Biochem. Z.*, **277** (1935), 111.
(9) *Biochem. Z.*, **279** (1935). 131.
(10) A. Purr, *Biochem. J.*, **29** (1934), 5.
(11) M. Bergmann und W. F. Ross, *J. Biol. Chem.*, **111** (1935), 659.

Carbonylreagenzien auf Papain ist eine Zeitreaktion und wird erst beim tagelangem Stehen vollständig. Beim 2–3 tägiger Einwirkung der Reagenzien wurde nicht nur die Peptidasewirkung, sondern auch die Wirkung der Gelatinespaltung (Proteinase) fast völlig gehemmt, und durch Cyanwasserstoff oder Benzaldehyd konnte keine Reaktivierung erzielt werden. Nach den obigen Resultaten müsste man zu einem von der Bergmannschen Ansicht verschiedenen Schluss kommen, dass nämlich nicht nur der Papainpeptidase-, sondern auch der Proteinase-anteil des Papains ein Carbonylgruppen enthaltender Komplex ist.

Und die Hemmung durch Dimethylbarbitursäure lehrt uns, dass die Carbonylgruppe, die mit der Aktivität des Papains in engem Zusammenhang steht, zu einer Aldehydgruppe gehört, weil Dimethylbarbitursäure nur mit Aldehyden, aber nicht mit Ketonen reagiert.[12]



Die entstandenen Aldehyd-dimethylbarbitursäuren sind gelb gefärbt, wenn die Aldehyd aromatisch oder Furanderivate sind. Die Papain-dimethylbarbitursäurelösung färbt sich allmählich beim Stehen und die Hemmung schreitet parallel mit der Vertiefung der Farbe fort.

Mein Papainpräparat ist durch proteolytische Enzyme schwer verdaubar. Bei der Trypsin- und Pepsin-wirkung war eine kleine Zunahme des COOH zu beobachten, während sich die Aktivität des Enzyms nicht verminderte.

Ob Papain ein Protein ist oder nicht, kann man jetzt noch nicht mit Sicherheit sagen. Jedenfalls ist aber Papain eine hochmolekulare Substanz und vielleicht ein spezielles Protein, das eine Aldehyd-gruppe trägt.

Beschreibung der Versuche.

1. Reinigung des Papains. 50 g. Handelspapain wurden mit 500 c.c. destilliertem Wasser durchgeschüttelt, 4–5 Stunden bei Zimmertemperatur stehen gelassen, abzentrifugiert und die klare Lösung mittels einer Kollodiumhülse 70 Stunden lang gegen destilliertes Wasser dialysiert. Aus der Innenflüssigkeit wurden durch Zusatz von Methanol 10.7 g. eines Niederschlags gewonnen, der relativ geringe Aktivität aufwies, aber durch HCN stark aktiviert wurde.

(12) S. Akabori, *Ber.*, **66** (1933), 139.

Tabelle 1.

Ansatz: N/5 Acetatpuffer ($pH = 5$) 1 c.c.+5%ige Gelatinelösung 5 c.c. (oder 1/5 Mol Hippuramidlösung 5 c.c.)+5%ige Papainlösung 1 c.c.

COOH Zuwachs (c.c. N/5 KOH) bei 36°						
	Gelatine			Hippuramid		
Stunde	1	4	24	1	4	24
Gereinigtes Papain	0.44	0.98	1.68	0.02	0.04	0.84
HCN (16 mg.)	1.66	2.46	3.42	0.10	0.48	1.26

2. Analysen des Papains. (a) *Gesamt-Stickstoff nach Kjeldahl.* Gef.: N, 15.10, 15.05, 14.92; mittlerer Wert, 15.02%.

(b) *Amino-Stickstoff nach Van Slyke.* Gef.: NH_2-N, 2.14, 2.45, 2.23; mittlerer Wert, 2.27%.

$$\frac{NH_2\text{-}N}{N} = 0.144....$$ etwas höher als gewöhnliche Proteine.

(c) *Bestimmung von Tryptophan.* Es ist heute eine ganze Anzahl von Methoden zur Bestimmung von Tryptophan unter verschiedenen Bedingungen bekannt. Es sei an die kolorimetrische von J. Tillmans und A. Alt[13] erinnert, die auf Verwendung von Formalin in Gegenwart von Schwefelsäure beruht, an die jodometrische von A. Homer[14], die auf der Bildung des Octabromtryptophans basiert. C. Itagaki und R. Masayama[15] verbesserten die Methode von Tillmans und Alt mit Hilfe eines Stufenphotometers. Diese von Itagaki und Masayama angegebene Methode wird als sehr zweckmässig empfohlen.

Ausführung: Zu 1 c.c. der zu bestimmenden Enzymlösung (geeigneter Konzentration), die sich in einem 20 c.c.-Messkolben befindet, fügt man 2 Tropfen einer 2%igen Formalinlösung hinzu und füllt mit 66%iger Schwefelsäure genau bis zur Marke auf. Nachdem man die Mischung 5 Minuten stehen gelassen hat, (dabei zeigt die Lösung eine Gelbfärbung), pipettiert man eine Probe in eine Küvette von geeignetem Inhalt und bestimmt den Extinktionskoeffizienten K mittels eine Stufenphotometers (als Filter Zeiss S 47 verwendet). Als Kontrolllösung wurde ein Probelösung ohne Zusatz von Formalinlösung verwendet. Die Berechnung des Tryptophangehaltes erfolg mit Hilfe einer Kurve, durch die vorher der Zusammenhang zwischen Tryptophangehalt und Extinktionskoeffizient festgestellt worden ist. (Gef.: Tryptophan, 3.34, 3.57, 3.40; mittlerer Wert, 3.43%.)

Herrn Dr. R. Masayama im medizinischen Institut der hiesigen Universität, unter dessen freundlicher Leitung diese Bestimmungen durchgeführt worden sind, bin ich sehr verbunden.

3. Einfluss von verschiedenen Reagenzien auf Papain. Es wurden jeweils 0.2 g. Reagens in 5 c.c. 5%iger Papainlösung aufgelöst (4%ige Probelösung). Dann wurde nach einer bestimmten Zeitspanne 1 c.c. abpipettiert und die Aktivität geprüft.

(13) *Biochem. Z.*, **164** (1925), 135.
(14) *J. Biol. Chem.*, **22** (1915), 369.
(15) *Mitt. Med. Ges. Osaka*, **35** (1936), 1743.

Tabelle 2. Einfluss von verschiedenen Reagenzien auf Papain.

Nr.	Reagenzien (%)		Wirkungsdauer von Reagens auf Papain bei Zimmertemperatur (Stunden)	COOH Zuwachs (c c. N/5 KOH) bei 36°					
				Gelatine			Hippuramid		
				1 St.	5 St.	24 St.	1 St.	5 St.	24 St.
1	NH_2OH	4	15 auf HCN-Papain	—	1.12	1.51	00	00	0.03
			ohne Reagens	—	1.96	2.76	—	0.37	0.78
2	NH_2OH	4	24 auf Papain	0.34	0.36	0.57	00	00	00
3	NH_2OH	10	52 auf Papain	00	0.08	0.13	00	00	00
			ohne Reagens	1.54	2.38	3.23	0.22	0.84	1.36
4	NH_2OH + C_6H_5CHO	8	120 auf Papain	00	00	00	—	—	—
			24 auf Papain	00	00	00	—	—	—
			ohne Reagens	—	1.19	2.27	—	—	—
	NH_2OH + HCN	4	120 auf Papain	00	00	00	—	—	—
			48 auf Papain	00	00	00	—	—	—
5	CH_3COCH_3	4	12 auf Papain	1.52	2.18	2.91	0.39	0.90	1.13
			ohne Reagens	1.54	2.38	3.23	0.22	0.84	1.36
6	$C_6H_5NH_2$	4	0.5 auf Papain	1.30	1.78	2.02	0.12	0.40	0.92
			ohne Reagens	1.70	2.20	3.09	0.24	0.60	1.22
7	$NaHSO_3$	4	24 auf HCN-Papain	0.41	0.59	2.26	—	—	—
			ohne Reagens	1.56	2.09	2.82	—	—	—
8	$NaHSO_3$	4	24 auf Papain	0.31	0.63	1.19	—	—	—
			ohne Reagens	1.21	1.54	1.90	—	—	—
9	$NaHSO_3$	4	120 auf Papain	00	0.02	0.04	—	—	—
			ohne Reagens	—	1.10	2.26	—	—	—
10	$NaHSO_3$ + CH_3COCH_3	4	24 auf Papain	0.29	0.52	1.23	—	—	—
			24 auf Papain	0.38	1.42	1.93	—	—	—
			ohne Reagens	0.96	1.68	2.48	—	—	—
11	$C_6H_5NHNH_2$	4	24 auf Papain	0.05	0.31	—	—	—	—
			ohne Reagens	1.08	1.52	—	—	—	—
12	$C_6H_5NHNH_2$ + C_6H_5CHO	4	68 auf Papain	00	0.10	—	—	—	—
			22 auf Papain	00	00	—	—	—	—
			ohne Reagens	0.76	1.34	—	—	—	—
13	$C_6H_5NHNH_2$	4	92 auf Papain	00	00	—	—	—	—
			ohne Reagens	0.56	1.36	—	—	—	—
14	D. B. S.*	4	40 auf Papain	0.27	0.67	1.11	00	00	00
			ohne Reagens	0.61	1.44	2.05	0.02	0.08	0.44
15	D. B. S.	4	sofort nach Zusatz	1.41	1.96	2.23	—	—	—
			ohne Reagens	1.49	1.88	2.23	—	—	—
16	D. B. S.	4	40 auf HCN-Papain	1.49	1.88	2.11	—	—	—
			ohne Reagens	1.59	2.19	2.87	—	—	—
17	D. B. S.	4	120 auf Papain	0.24	0.48	0.56	—	—	—
			ohne Reagens	0.89	1.57	2.31			

* D. B. S. = Dimethylbarbitursäure.

Bergmann[16] sagt, dass bei der Inaktivierung durch Phenylhydrazin bei einer Konzentration von 0.03 millimol Reagens pro c.c. einer 0.45%igen Papainlösung die maximale Schädigung erreicht wird und eine weitere Zunahme der Phenylhydrazinkonzentration keine stärkere Hemmung mehr erzeugt. Und er hat daher angenommen, dass die Verdauung von Gelatine durch HCN-Papain über zwei verschiedene enzymatische Prozesse geht. In diesem Zusammenhang habe ich festgestellt, dass diese Aktivitätshemmung durch Vergiftung des Papains eine Zeitreaktion ist, dass also durch 68-stündige Einwirkungsdauer von Phenylhydrazin die Aktivität des Papains fast völlig beseitigt werden kann.

Dimethylbarbitursäure ist etwas schwerer zu kondensieren mit Papaincarbonyl als allgemeine Carbonylreagenzien, und deshalb ist zur vollkommenen Hemmung durch Dimethylbarbitursäure etwas längere Zeit erforderlich als im Fall des Hydroxylamins, Hydrazins und Phenylhydrazins.

Tabelle 3. Zeitlicher Verlauf der Inaktivierung durch Hydroxylamin, Hydrazin und Phenylhydrazin.

	COOH Zuwachs (c.c. N/5 KOH)		
Stunde	NH_2OH	NH_2NH_2	$C_6H_5NHNH_2$
0	1.51	1.51	1.51
0.5	1.04	1.25	0.36
1	—	1.06	—
3	0.62	0.70	0.20
6	0.38	0.46	0.10
23	0.18	0.12	0.02

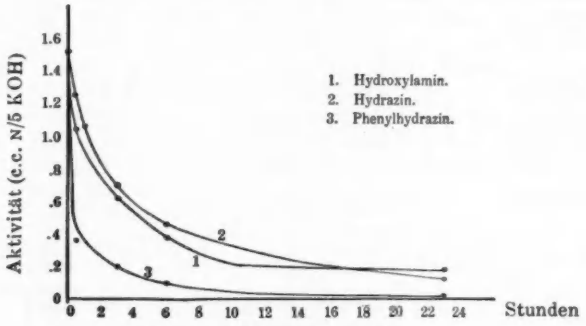


Abb. 1. Hemmungskurven.

Zu einer Lösung von 0.6 g. Inaktivator in 15 c.c. destilliertem Wasser, das nötigenfalls vorher auf etwa $pH = 5.0$ eingestellt worden ist, setzt man 15 c.c. 5%ige Papainlösung zu. Nachdem die Mischung eine bestimmte Zeitspanne bei 36° verblieben ist,

(16) M. Bergmann und W. F. Ross, *J. Biol. Chem.*, **114** (1936), 717.

pipettiert man 2 c.c. ab, fügt 5 c.c. 5%ige Gelatine und 3 c.c. N/5 Acetatpuffer hinzu und titriert sie. Die Resultate sind in den Tabelle 3 und Abb. 1 angegeben.

4. Einwirkung proteolytischer Enzyme. Ich prüfte die Beständigkeit von gereinigtem Papain-präparat gegenüber der Wirkung von Pepsin und Trypsin-kinase, wobei sich in keinem Falle irgendwelche messbare Aktivitäts-einbusse bemerken liess.

Verdauung durch Trypsin-kinase und Pepsin. (Tabelle 4.)

Tabelle 4.

Ansatz: A. 5%ige Papain-lösung (pH = 8) 5 c.c.+N Phosphatpuffer (Na_2HPO_4) 1 c.c. +Trypsin-kinase 2 c.c. bei 30°; B. 5%ige Papain-lösung 2 c.c.+N Glykokollmischung (pH = 1.93) 1 c.c.+Pepsin (1%) 1 c.c. bei 36°.

COOH Zuwachs (c.c. N/5 KOH)				
Stunde	1/3	1	4	24
Trypsin-kinase	0.08	0.06	0.19	0.21
Pepsin	—	0.06	0.10	0.28

Aktivität des durch Trypsin-kinase und Pepsin verdauten Papains gegenüber Gelatine. Kontrollversuch: Nachdem die Mischung von 5 c.c. einer 5%igen Papain-lösung und 1 c.c. N Phosphatpuffer jeweils eine entsprechende Anzahl Stunden bei 30° stehen gelassen worden war, wurden 2 c.c. Trypsin-kinase zugesetzt, sofort auf pH = 5.0 eingestellt und die Aktivität gegenüber Gelatine (5%ige Gelatine 5 c.c.) während einer Stunde bei 36° geprüft. Beim Pepsin: 5%iges Papain 2 c.c., N Glykokollmischung (pH = 1.93) 1 c.c. und 1%iges Pepsin 1 c.c. In gleicher Weise ausgeführt. Die Versuchsergebnisse sind in Tabelle 5 zusammengestellt.

Tabelle 5.

	COOH Zuwachs (c.c. N/5 KOH)			
	Stunde	1	4	24
Kontroll-versuch	Trypsin-kinase	1.66	1.64	—
	Pepsin	1.20	1.26	1.18
Haupt-versuch	Trypsin-kinase	1.57	1.58	—
	Pepsin	1.22	1.30	1.18

Es sei mir an dieser Stelle erlaubt, Herrn Prof. S. Akabori für die Überlassung dieser Arbeit, sowie für Anregungen und Ratschläge meinen verbindlichsten Dank auszusprechen.

Chemisches Institut der Kaiserlichen Universität zu Osaka.

The Dielectric Constant of Cetyl Alcohol Near its Melting Point.

By Ken-iti HIGASI and Masaji KUBO.

(Received May 31st, 1937.)

Using a heterodyne beat apparatus[1] of 3000 kilocycles, we studied the temperature dependence of the dielectric constant of cetyl alcohol.

The dielectric constant of this substance increases on solidification, passes through a maximum at a temperature a little below the melting point and then drops to a nearly constant value at lower temperatures, which is the same order of the magnitude as non-polar substances (Cf. Table 1 and the figure).

Table 1.
The Dielectric Constant of Cetyl Alcohol ($\lambda = 100$ m.)

t (°C.)	ε	t (°C.)	ε	t (°C.)	ε (liquid)
−13.5	2.55	25.0	4.19	50.0	3.86
−12.6	2.56	29.7	5.65	50.0	3.86
3.5	2.77	29.8	5.65	57.0	3.74
4.2	2.75	34.9	5.70	57.1	3.74
13.8	2.85	35.0	5.70	63.7	3.65
14.1	2.85	42.0	5.27	64.0	3.64
20.8	3.25	42.0	5.27		
20.9	3.28	45.4	4.81		
25.0	4.10	45.7	4.78		

Methyl alcohol[2] and normal long chain ketones[3] are reported to show a considerable increase in the dielectric constant in a wide range below their melting points. But any of them differs from cetyl alcohol in that it gives lower dielectric constant in solid state than in liquid state. Piekara's observation[4] on oleic acid reveals a feature similar to that by our experiment, but in the case of cetyl alcohol it is exhibited much more distinctly.

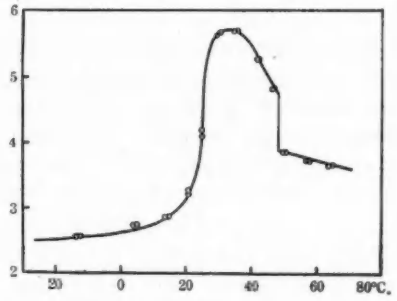
(1) The same apparatus used in the determination of the dielectric constant of gases, was employed in the present work with a slight modification. See M. Kubo, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **26** (1935), 242; **27** (1935), 65.

(2) C. P. Smyth and S. A. McNeight, *J. Am. Chem. Soc.*, **58** (1936), 1597.

(3) A. Müller, *Proc. Roy. Soc.* (London), A, **158** (1937), 403.

(4) B. Piekara, *Physik. Z.*, **37** (1936), 624.

In Table 2, the dipole moment[5] of this substance in solution are recorded. Excepting the values in hexane solution, which are not free from the errors of association, the observed moments are remarkably constant. It is clear from this that no abnormality occurs in the dipole moment in the range of the temperature observed.



Temperature dependence of the dielectric constant of cetyl alcohol

Table 2. The Dipole Moment of Cetyl Alcohol

t (°C.)	benzene		hexane	
	P	μ	P	μ
20	140.0	1.70	114.3	1.30
30	137.3	1.70		
40	135.8	1.70	122.0	1.48
50	132.7	1.68		
60	131.8	1.69	125.0	1.58

$P_E + P_A = P_{solid}$[6] $= 78.5$ c.c.

According to the X-ray studies by Malkins,[7] two lattice constants are given to this alcohol and a transition between them is supposed to occur when it is near room temperature. If this observation be correct, has this transition any relation with the observed anormaly in the dielectric constant?

No satisfactory explanation can be given at the present stage of the investigation. And in the following paper a fuller discussion on this problem will be given.

In conclusion, the writers wish to express their cordial thanks to Prof. M. Katayama and Prof. S. Mizushima for their kind guidance and encouragement throughout this experiment.

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(5) From the result of our previous work, which was published in Japanese: K. Higasi, *Bull. Inst. Phys. Chem. Research* (Tokyo), **12** (1933), 780.

(6) P_{solid} used here is the polarisation obtained by using an apparatus of shorter wavelength at very low temperature.

(7) T. Malkins, *J. Am. Chem. Soc.*, **52** (1930), 3739.

A Note on the Cannizzaro Reaction.

By Yoshiyuki URUSHIBARA and Matsuji TAKEBAYASHI.

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In the course of the investigation on the effect of oxygen and ferromagnetic metals on the addition of hydrogen bromide to allyl bromide, the authors[1] came to suspect that the effect of peroxides on the Cannizzaro reaction observed by M. S. Kharasch and M. Foy[2] was really caused by molecular oxygen, because molecular oxygen was found the active catalyst influencing the direction of addition and the yield of the products in the reaction of hydrogen bromide with allyl bromide although the experimental evidence so far obtained could not totally exclude the possibility that peroxides were active also as such.[3] But the authors'

Series of experiment	No. of exp.	Added	Extent of Cannizzaro reaction (%)
I Peroxide-free benzaldehyde	1	None	10
	2	None	9
	3	Hydroquinone, 0.1 g.	8
II Purified benzaldehyde, exposed to air for 5 minutes	4	None	53
III Commercial benzaldehyde	5*	None	76
	6	None	83
IV Peroxide-free benzaldehyde	7	Reduced iron, 1.5 g.	10
	8	Reduced nickel, 1.5 g.	11
	9	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	9
	10	Reduced nickel, 1.5 g. Hydroquinone, 0.1 g.	10

* Reaction time: 2 hours.

(1) This Bulletin, **12** (1937), 54.
(2) *J. Am. Chem. Soc.*, **57** (1935), 1510.
(3) This Bulletin, **11** (1936), 798; **12** (1937), 133, 173.

expectation has not been proved, and the Cannizzaro reaction may be more reasonably regarded as a chain reaction in which the peroxide of the aldehyde concerned, even though present in very minute traces, plays an important part. A support to such an interpretation is given by the fact that benzaldehyde has been found extremely sensitive to peroxide formation even in the dark,[4] and that the Cannizzaro reaction does not undergo even the slightest influence of ferro-magnetic metals, which cause an effect quite similar to that of oxygen, in the addition of hydrogen bromide to allyl bromide. The experimental results are summarised in the accompanying table. Benzaldehyde (10 c.c.) was shaken with an excess of aqueous potassium hydroxide (13.8 N, 10 c.c.) in vacuum in the dark at room temperature for three hours, and the extent of Cannizzaro reaction was determined from the alkali consumed.

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(4) Allyl bromide does not form peroxide in the dark, this Bulletin, **11** (1936), 798.